University of Alberta

Department of Chemical and Petroleum

Engineering

PYROLYSIS OF NORMAL BUTANE AT

HIGH TEMPERATURE

by

Angus R. S. Leitch

, Alberta.   April 20, 1956.

THE UNIVERSITY OF ALBERTA

PYROLYSIS OF BUTANE AT HIGH TEMPERATURE

A DISSERTATION
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
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FACULTY OF ENGINEERING
DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

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Angus R. S. Leitch

EDMONTON, ALBERTA,
April 20, 1956.

Abstract:

        The pyrolysis of normal butane at high temperature was investigated for the purpose of evaluating the effects of temperature, space velocity, and the concentration of hydrocarbons in the feed gas on the product yield.

        It was found that the main products of decomposition at the temperatures investigated were ethylene, acetylene, methane, carbon and hydrogen. Very small quantities of higher unsaturates were formed. Only ethylene and acetylene were considered potentially commercial products.

        An increase in space velocity was found to increase the relative yield of ethylene. At high dilution ratios, the ratio of acetylene to ethylene was increased.

        The physical properties of the diluent gas were found to influence the decomposition; a gas that was highly absorbent to radiant energy tended to increase the yield of ethylene while holding the yield of acetylene constant.

        Chemically, some possibility of a commercial installation of the type investigated exists, on the basis of competition with those processes now in use. Pyrolysis of butane in a natural gas stream is thought to be a logical and desirable method to produce ethylene and acetylene in Alberta.

Acknowledgement

during the course of the problem.

   To all these I extend my grateful thanks.

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Symbols and Definitions

Symbol	Definition
c	Number of carbon atoms in the molecule.
d	Diameter of reactor tubes (ins.)
Δ	Change in variable during a process.
E	Overall expansion of the feed through the reactor.
E_c	Expansion of the carbon compounds.
E_r	Expansion of the reactants.
F	Moles of substance per 100 moles of feed.
f	Composition of the feed gas (mole fraction)
H	Molal enthalpy of a substance BTU/lb. mole.
h	Number of hydrogen atoms in molecule.
$K_a = K_p$	Equilibrium ratio.
k	Thermal conductivity BTU/(hr.ft.^{2} $^{\circ}$F in)
l	Thickness of tube wall (in)
L	Length of reactor tube (in.)
M	Moles product per 100 moles feed (corrected to nitrogen balance)
M'	Moles product per 100 moles feed
m	Air free analysis (mole fraction)
n	Analysis of gaseous products (mole fraction).
p	Total pressure
p	Partial pressure
Q	Heat flux. BTU/hr.

Symbol	Definition
R	Universal gas constant
T	Absolute temperature $^\circ R$
t	Temperature $^\circ F$
Y	Product yield, moles per 100 moles of butane.
y	Product yield, moles per 100 moles of feed.
y_2	Product yield, moles per 100 equivalent moles of C_2.

Subscripts refer to the substance, group of substances or condition of the main symbol.

Subscript	Definition
a	Acetylene
b	Butane
c	Carbon containing substance
e	Ethylene
g	Gas
h	Hydrogen
i	Inner surface
m	Methane
n	Nitrogen
n.g.	Natural gas
O	Oxygen on outside surface.
R	Based on reacting butane
r	Over the reaction
T	Reaction temperature $^\circ R$
t	Room temperature

I.   Introduction

During the past three-quarters century, the thermal decomposition of hydrocarbons has been investigated by a large number of workers, both to determine the mechanism by which the phenomenon occurs, and to develop commercially feasible methods for exploitation.   Any study of these pyrolytic reactions must refer to some extent to the reactions of similar compounds within the homologous series.   From the viewpoint of the saturated series, it is apparent that only two possible primary reactions occur;   a dehydrogenation or a split in the carbon chain.

Cracking petroleum fractions to form gasoline is not a new science, and has been in use for a great many years.   Substances such as heavy crude have yielded up to eighty-five per cent gasoline fractions compared with possibly thirty per cent previous to cracking operations.   Although the modern methods of catalytic cracking could not be viewed as strictly pyrolytic in nature, yet the fundamental reactions were the results of thermal decomposition.   Cracking petroleum to form blending stock for gasolines was a necessary adjunct to the increasingly high compression ratios of modern engines.

Natural gas hydrocarbons,—methane, ethane, propane and butane-provide an immense potential source

of raw material for industrial exploitation. These
hydrocarbons have, until recently, been used primarily
as fuel. In Alberta, the development of a natural
gas pipeline across the width of the continent has
been proposed to market the methane-rich fractions of
natural gas. With the sale of tremendous volumes of
natural gas, large amounts of natural gas liquids will
become available. For economic reasons as well as
conservation of our natural resources, these liquids
must find a suitable market. Many uses for propane
have been suggested, as a chemical raw material, and
as domestic and motor fuel. The use of butane as a
fuel is limited by the low ambient temperatures
encountered in Alberta, and the petrochemical industry
seems to offer the most promising market.

Alberta has already secured about forty
percent of the petrochemical investment in Canada (18)
and it is not likely that this share will decrease.
An abundance of propane and particularly butane has
been anticipated. A plant for production of butadiene
from butane which would use about 70 thousand pounds of
normal butane per day has been reported to be in the
planning stage, but it has been estimated that the
total butane production in Alberta will reach about
160 thousand pounds per day within five years after

gas export has begun.   Butane is already being used
in Alberta as a raw material for the manufacture of
cellulose acetate, propionaldehyde, acetic acid, and
acetic anhydride.   Butane is also a natural source for
the manufacture of chemical intermediates such as
acetylene, ethylene and propylene.   The cost of butane
has been estimated from about 1.0¢ per lb. carbon
content to about 0.7¢ per lb. carbon content, compared
to about 0.4¢ per lb. carbon content from methane and
about 1.4¢ per lb. carbon content for propane.   For an
average price of 0.8¢ per lb. carbon content, the use
of butane may be competitive as a raw material when
its greater chemical reactivity is considered.

Normal butane probably presents a greater
marketing problem than isobutane (which is a source
for alkylate for motor and aviation gasoline).

For the reasons outlined above, this investi-
gation was confined to the reactions of normal butane.
A study of the literature and one experimental run
was sufficient to demonstrate the need for either a
diluent gas or low total pressure to increase the yield
of the desired products.   From both investigational
and practical viewpoints, the use of a dilute gas
seemed to be preferable.

The choice of nitrogen as diluent in these
investigations followed directly from these considerations:

Nitrogen is inert, will not enter the reaction, and is
readily available in comparatively pure form. Natural
gas was chosen for investigation, since supplies
containing the desired quantities of propane and butane
are plentiful in Alberta.

II. Theoretical Background

a. Decomposition Products and Mechanism

Extensive investigations of the pyrolysis of hydrocarbons have been made, and are recorded in the literature. These investigations had as their aim two alternative objectives:

1. To gather data concerning the fundamental reactions of hydrocarbons, and

2. To determine the possible commercial potential of the decomposition processes.

The variables under investigation for a particular feed were temperature, pressure, and contact time. For the studies of the fundamental reactions, the time of reaction was often long, the reaction being relatively slow at the temperature used. Often, the reaction at initial conditions was quite different from that taking place after some decomposition had occurred. Conditions were often deliberately chosen to limit the velocity of the reactions, to allow the course of the reactions to be followed.

Studies concerning commercial application of pyrolysis were carried out using specialized equipment. The overall reaction was studied, and the variables controlled to yield optimum desired product. Little systematic information concerning the effect of specific variables was offered.

Because of the analytical problems involved, investigations into the basic reactions of the hydrocarbons have been restricted to a study of the simpler hydrocarbons. For this reason the literature deals with methane and ethane quite thoroughly, while some data on propane and butane are available, but to a much lesser degree.

The pyrolysis of butane at low temperature has been discussed at some length. Essentially, the products of initial decomposition were propylene, methane, ethylene, ethane, butylene and hydrogen. The relative yields were dictated by pyrolysis conditions. An attempt was made by Schneider and Frolich (23) to deduce a general decomposition mechanism from the decomposition of propane by successive determinations of the primary decomposition for each step at $1200^\circ F$ to $1400^\circ F$.

$$C_3H_8 \longrightarrow C_2H_4 \xrightarrow{\text{Rapid}} C_4H_6 \xrightarrow{C_2H_4} C_6H_6$$

$$C_3H_6 \qquad\qquad C_6H_8 \xleftarrow{C_2H_4}$$
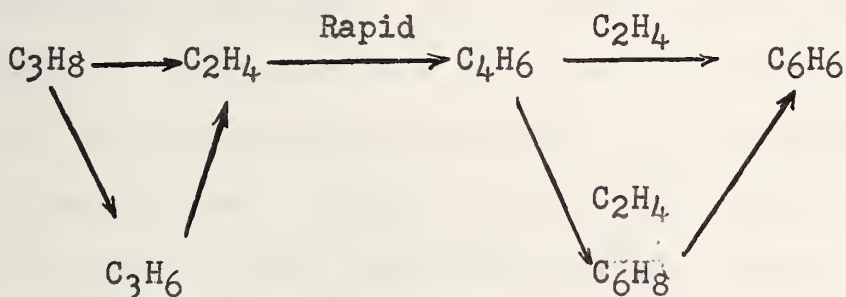
Conditions for each of the steps were deduced by attempting to approximate the partial pressures of feed gas at the time of initiation, thereby reproducing the mechanism in a stepwise fashion:

i.e.
$$C_3H_8 \rightleftharpoons C_2H_4 + CH_4 \qquad \text{1 atm.}$$
$$2C_2H_4 \longrightarrow C_4H_6 + H_2 \qquad \text{1/5 atm.}$$
$$2C_3H_6 \longrightarrow C_4H_6 + C_2H_6 \qquad \text{1/5 atm.}$$
$$C_4H_6 \longrightarrow C_2H_4 + C_6H_6 + 2H_2 \qquad \text{1/5 atm.}$$
$$C_4H_6 \longrightarrow C_2H_4 + C_6H_8 + H_2 \qquad \text{1/5 atm.}$$
$$C_6H_8 \longrightarrow C_6H_6 + H_2$$
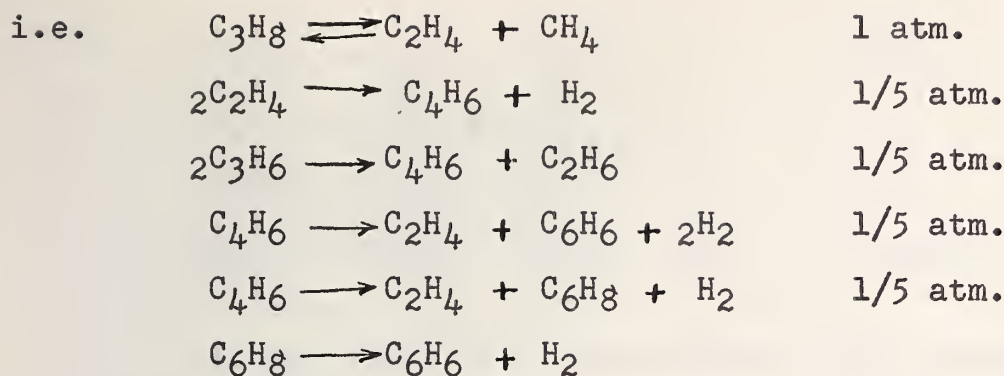
Qualitatively, the reactions would follow the paths indicated, although the relative reaction rates become sensitive to composition, and the relative importance of the reactions need not be as shown.

Hague and Wheeler (10) found butadiene at 1380°F to 1560°F and a space velocity of 30 sec.$^{-1}$ and atmospheric pressure. Higher olefins were present in significant amounts at 1200°F, but decreased markedly as the temperature increased. An inverse relation between contact time and temperature was shown and the effect of the extent of decomposition at 1100°F on the products formed was demonstrated. More propylene than ethylene was found during the first 30% decomposition; but at 80% reaction, ethylene predominated. Similar products were produced at 750°F and 1100°F by varying the contact time.

It was shown by Hague and Wheeler and also by Hurd and Pilgrim (11) that the primary reaction for butane at these temperatures could be satisfactorily explained by the equations:

$$C_4H_{10} \rightarrow C_2H_4 + C_2H_6 \qquad \text{H and W} \atop 40\%$$

$$C_4H_{10} \rightarrow C_3H_6 + CH_4 \qquad\qquad 35\%$$

$$C_4H_{10} \rightarrow C_4H_8 + H_2 \qquad\qquad 20\%$$

$$2C_4H_{10} \rightarrow C_3H_8 + C_4H_8 + CH_4 \qquad \text{(small)}$$
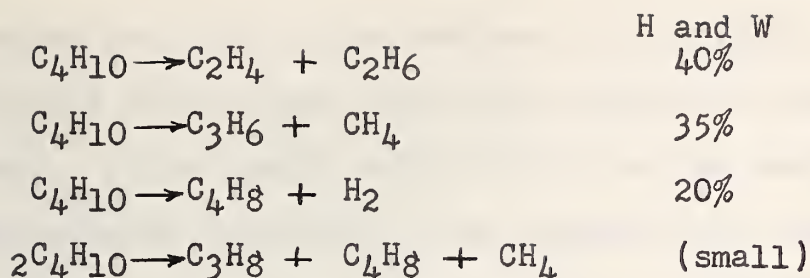
It has been amply demonstrated that kinetically the primary reactions of hydrocarbons are reasonably satisfied by the first order rate expression at incipient decomposition and low pressures (12)(13)(23). An unusual pressure sensitivity has been observed, however, which suggests that the reaction does not actually proceed according to the ordinary concept of a unimolecular decomposition. Hague and Wheeler have suggested the possible existence of "residues", or free radicals which behave in a manner not unlike that of a highly active molecule, and/or become the initiating step in a free radical chain.

Steacie (25)(3) has proposed a mechanism for the decomposition of ethane by free radical chains that not only satisfies the apparent first order relationship, but explains the deviation from first order behaviour. at very high and very low pressure.
Ethane was chosen for study since it is the simplest member of the paraffin series that contains a carbon-carbon bond, and is therefore more representative of the series than methane. Furthermore, since the radicals formed are simple and relatively well known,

the mechanism could be better defined (both methyl and
ethyl radicals having been previously studied in the
literature).   Bond energy calculations may be used to show
that the preferred initiation step produces only the
methyl radical; thus, the kinetics study is greatly
simplified.

The overall rate equation for the
decomposition of ethane to ethylene and hydrogen

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$
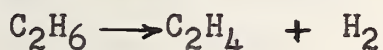
was found from a study of all available kinetic data
to be

$$\log_{10}k = 15.09 + 74000/(2.3RT)$$

where k is the apparent first order reaction constant
in reciprocal seconds.   The reaction is approximately
first order, but the rate constant was found to fall
off at low ethylene concentrations and high conversions.
The products were almost all ethylene and hydrogen in
equal proportions, with small amounts of methane and a
trace of aromatic liquid.

Since the reaction was strongly inhibited
by nitrous oxide and propylene, this suggests a chain
mechanism.   The following reaction steps were proposed
by Steacie (3):

$$C_2H_6 \rightleftharpoons 2CH_3 \qquad\qquad 1$$

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5 \qquad 2$$

$$C_2H_5 \longrightarrow C_2H_4 + H \qquad\qquad 3$$

$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \qquad 4$$

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \qquad 5a$$

$$H + C_2H_5 \longrightarrow C_2H_6 \qquad\qquad 5b$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \qquad\qquad 5c$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad\qquad 5d$$

$$H + CH_3 \longrightarrow CH_4 \qquad\qquad 5e$$

$$H + H \longrightarrow H_2 \qquad\qquad 5f$$
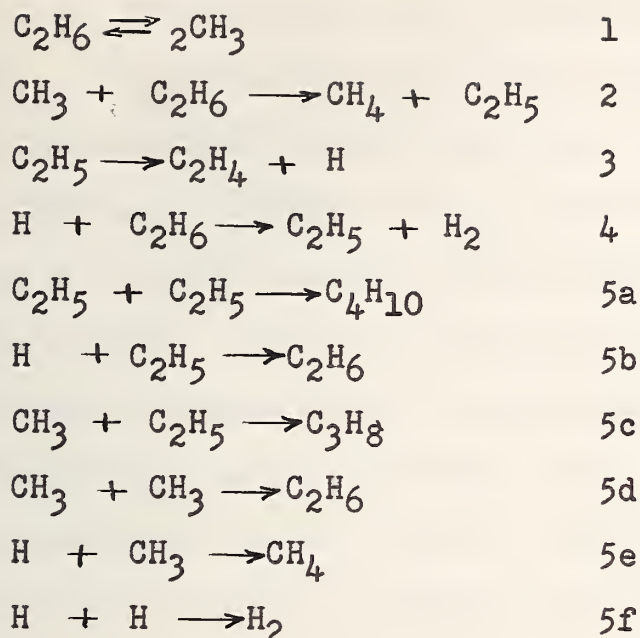
The rate equation for the above mechanism was presented:

$$\frac{d\,(C_2H_6)}{dt} = \frac{2^{\frac{1}{2}}\, k_1^{\frac{1}{2}}\, k_3\, (C_2H_6)^{\frac{1}{2}}}{k_5^{\frac{1}{2}}\, (1 + k_3/k_4\, (C_2H_6)\,)^{\frac{1}{2}}}$$

At high pressures and low temperature, a half order reaction was approximated. At higher temperature and lower pressure, a first order rate was found; at very low pressures, a 3/2 order was approximated. Some controversy over the mechanism of the inhibited decomposition still remains, but otherwise the mechanism is thought to be sound.

A mechanism of similar type may perhaps be operative in the decomposition of higher hydrocarbons, but the increased complexity of the initiation and propagation makes any quantitative predictions extremely difficult.

Rice (20) proposed the original general mechanism for the decomposition of hydrocarbons by free radicals. Initiation by a split to two radicals was assumed preferential at a carbon-carbon bond. Each radical was capable of carrying on the reaction. Decomposition of the more complex radicals was reported to take place rapidly, since the activation energy required for their decomposition was lower than that for the corresponding parent molecule. The simultaneous formation of the olefinic compounds was exothermic and the overall activation energy for the decomposition was reduced. Activation energies and reaction rates were postulated so that the calculated primary products of decomposition for normal butane at moderate temperature agreed quite well with the experimental data. Further decomposition and combination of primary products in a complex manner made kinetic studies difficult. In the case of butane, for instance, the mechanism would probable include radicals of the type CH_3, C_2H_5, C_3H_7, C_4H_9, and, if the reaction were carried out at very high temperatures, possibly CH_2, C_2H_4, etc.

At very short times of contact, the initial products of decomposition may be predicted with some certainty by consideration of the relative bond strengths, but for all except the extremely simple

molecules, the complete mechanism of decomposition
remains vague.

Prediction of a general mechanism for
decomposition has been attempted by several
investigators. Decomposition was postulated by
Linden (14) to proceed through free radical formation.
A great deal of experimental work was carried out on
various feed stocks (14) (15) (16), varying in nature
from methane to gas oil fractions, at pressure up to
5 atm. and temperatures in the order of 1500°F. The
reaction time was varied considerably, but was of the
order of 1 to 20 sec. It was noted that the gaseous
products were relatively independent of the feed stock.
Presence of large quantities of methane led to the
conclusion that methylene radicals were the most
important single factor in the mechanism. A steady
state concentration ratio of products for the system
ethane-ethylene-hydrogen computed from equilibrium
relationships was found to be approached after about
4 sec. residence time. The ethylene-acetylene
equilibrium was reportedly rapidly established (16).
The Linden mechanism is represented in part below:

$$\underline{C_nH_m} \qquad\qquad n \geqslant 2$$

$$\cdot CH_3, \ :CH_2, \ H_2\dot{C} - \dot{C}H_2, \ H\dot{C} = \dot{C}H$$

$$\big\updownarrow +H_2$$

$$C_2H_2 \rightleftharpoons H\dot{C} = \dot{C}H \rightleftharpoons H_2\dot{C} - \dot{C}H_2 \rightleftharpoons 2CH_2:$$

C_2H_4	C_3H_6	C_4H_8	C_iH_{2i}
$+ H_2$	$+H_2$	$+H_2$	$+H_2$
C_2H_6	C_3H_8	C_4H_{10}	$C_iH_{2i\ 2}$
$+ H_2$	$+H_2$	$+H_2$	$+H_2$
$2CH_4$	CH_4	CH_4	C_iH_{2i}
	$+$	$+$	$+$
	C_2H_6	C_3H_8	CH_4
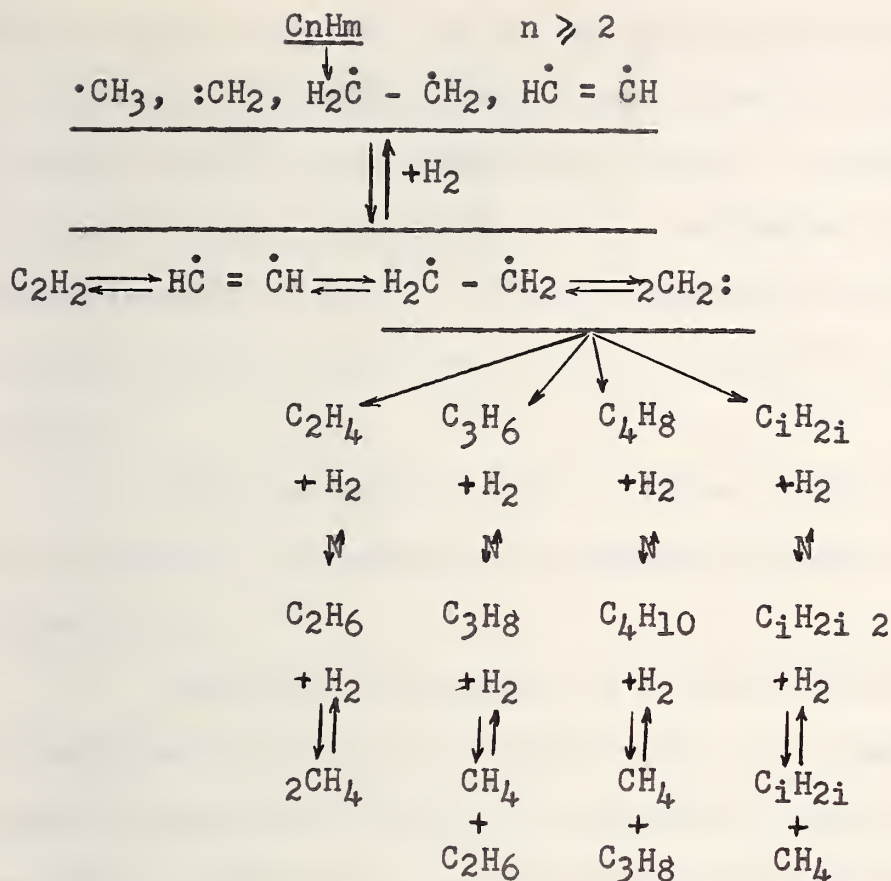
The original mechanism included the formation of butadiene, aromatics and napthalenes, but these have little significance in the present study. The individual steps were confirmed in a qualitative sense, but the mechanism was proposed chiefly as a guide for further study.

Reliable data explicitly concerned with the pyrolysis of normal butane were more difficult to find. The mechanisms previously discussed were not thought applicable directly to this problem since both the temperature and reaction time conditions were different from those proposed for this study. Tropsch and Egloff

(28) pyrolysed propane and butane in pythagoras tubes
at 2100°F and 2550°F, and reported a possible yield of
25 moles acetylene per 100 moles butane. A representation
of this data was prepared by Kramer and Happel (3) and
is represented in Fig. 1. Contact times for these
reactions were in the order of those reportedin this
thesis.

Some indication of the course of the reaction
can be gained from studies of related compounds at these
temperatures.

Pyrolysis of methane on a carbon rod was
investigated by Storch and Golden (27). At atmospheric
pressure and about 2730°F, at very short reaction time
the main products of decomposition were found to be
ethylene and acetylene. With increased velocity the
acetylene yield passed through a maximum. Carbon dioxide
and steam were used as diluent gases, and it was found
that at 1/10 atmosphere, with CO_2 diluent, 10% of the
diluent-free gas reacted to acetylene.

b.   Commercial Development

The production of acetylene has been expanded
enormously, and the search for a cheap means of manufac-
ture from hydrocarbons has been the center of a great
deal of development, using varied types of feed stock.
Since these data are essentially pyrolytic in nature, a

brief review is in order.

1. The Schoch process, at present in the
development stage, at the University of Texas (22),
utilizes a shaped electrical discharge through the gas,
creating an ambient temperature in the order of 570°F.
Arc "temperatures" are, of course, much higher (estimated
in the order of 2600°F); the products are acetylene and
methane (22) (24). Approximately 10% of the off-gases
are acetylene. High electrical energy requirements make
the process prohibitively expensive unless very cheap
power is available. (A similar process was developed
in Germany previous to and during World War II. This
process, the Huls process (17) was instrumental in
building the synthetic rubber industry in Germany.)

2. The Sachsse process makes use of partial
combustion to supply reaction energy to the hydrocarbon
(5) (6) (24). Either oxygen or air may be used in the
combustion, but the use of oxygen is favored since
product recovery is simplified. A mixture containing
an excess of hydrocarbon is passed through a special
burner, and the product gases are subjected to a water
spray quench. An estimated flame temperature of 2700°F
results using oxygen. The contact time is in the order
of 0.01 to 0.001 sec. Product gases are reported to
contain 3.5 percent acetylene when air is used, (24)
8.5 percent when oxygen is used. A valuable by-product
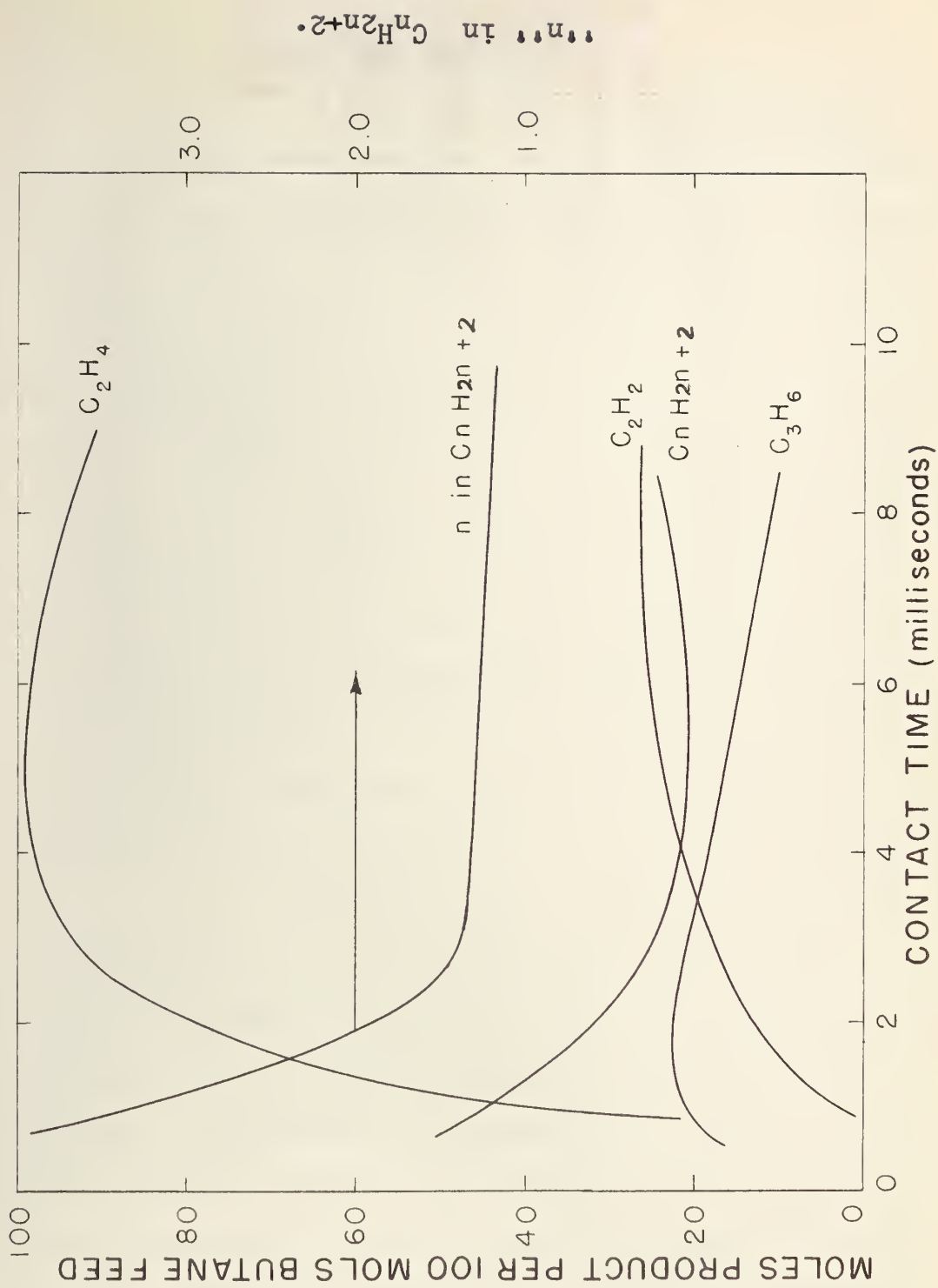
FIG. 1. PYROLYSIS OF NORMAL BUTANE AT 2100°F. and 50 mm.

from the work of TROPSCH and EGLOFF

of the process is a mixture of carbon monoxide and
hydrogen, known as "synthesis gas".

3.   The Wulff process (Koppers-Hasche) (4)
(7) was designed to produce a mixed product of ethylene
and acetylene, utilizing a regenerative type checkerwork
reaction chamber. One portion of the furnace provides
heat to the pyrolysis gases, the other tends to quench
the reaction during the pyrolysis cycle. Steam dilution
was used to allow low hydrocarbon pressure during the
reaction (an 8:1 steam to hydrocarbon ratio was suggested).
A temperature of 2200°F to 2400°F and reaction time in
the order of 0.03 sec. was used at atmospheric pressure.
The process has been successfully used for feed stocks
ranging from methane to butane. Yields in the order of
40-50 moles of acetylene per 100 moles of butane can be
expected, together with significant amounts of ethylene.

4.   The Hasche process (8) (9), in which heat
was supplied continuously through a reactor tube was
described in the patent literature. The process was used
extensively in development work leading to the Wulff
process, and operating conditions were similar to the
Wulff process. Preheat was supplied by the hot flue
gases passing over a stainless steel coil. Reaction
time was varied, but an average of 0.03 sec. would be
in order; reaction temperature was about 2100°F to 2550°F.
Preheat to about 1830°F lessened heat load on the reactor
tube, and also allowed the original feed to convert to

ethylene. High yields of acetylene and ethylene were reported. A representation of Hasche findings is shown on Fig. 2 for both propane and butane raw material.

In general, the products of decomposition may be controlled by proper balance of temperature, space velocity and partial pressure. At high temperature, the tendency to form aromatic tars may be overcome by the appropriate adjustment of space velocity. If an inert diluent is added to the reaction substance, the yield of gaseous products will increase, and that of liquids and carbon will decrease.

Of the processes described, the conditions existing in the Wulff process and the Hasche process were felt to most closely approximate the present work. The use of butane as feed stock for these processes gave some useful data; however, it should be stressed that those data reported for the Hasche process are patent data, while the data for the Wulff process were reported as average, and were incomplete for butane. In neither case were the reaction conditions completely specified.

c. Thermodynamic Considerations

At the reaction conditions of the proposed investigation, 2200°F to 2600°F, the paraffin hydrocarbons are inherently unstable, and at equilibrium

FIG. 2.

PRODUCT DISTRIBUTION FOR THE
HASCHE PROCESS

Legend:
Propane ————
Butane ————

CARBON MOLES / 100 MOLES FEED.

CRACKING TEMPERATURE °C.

VOLUMES / 100 VOLUMES FEED
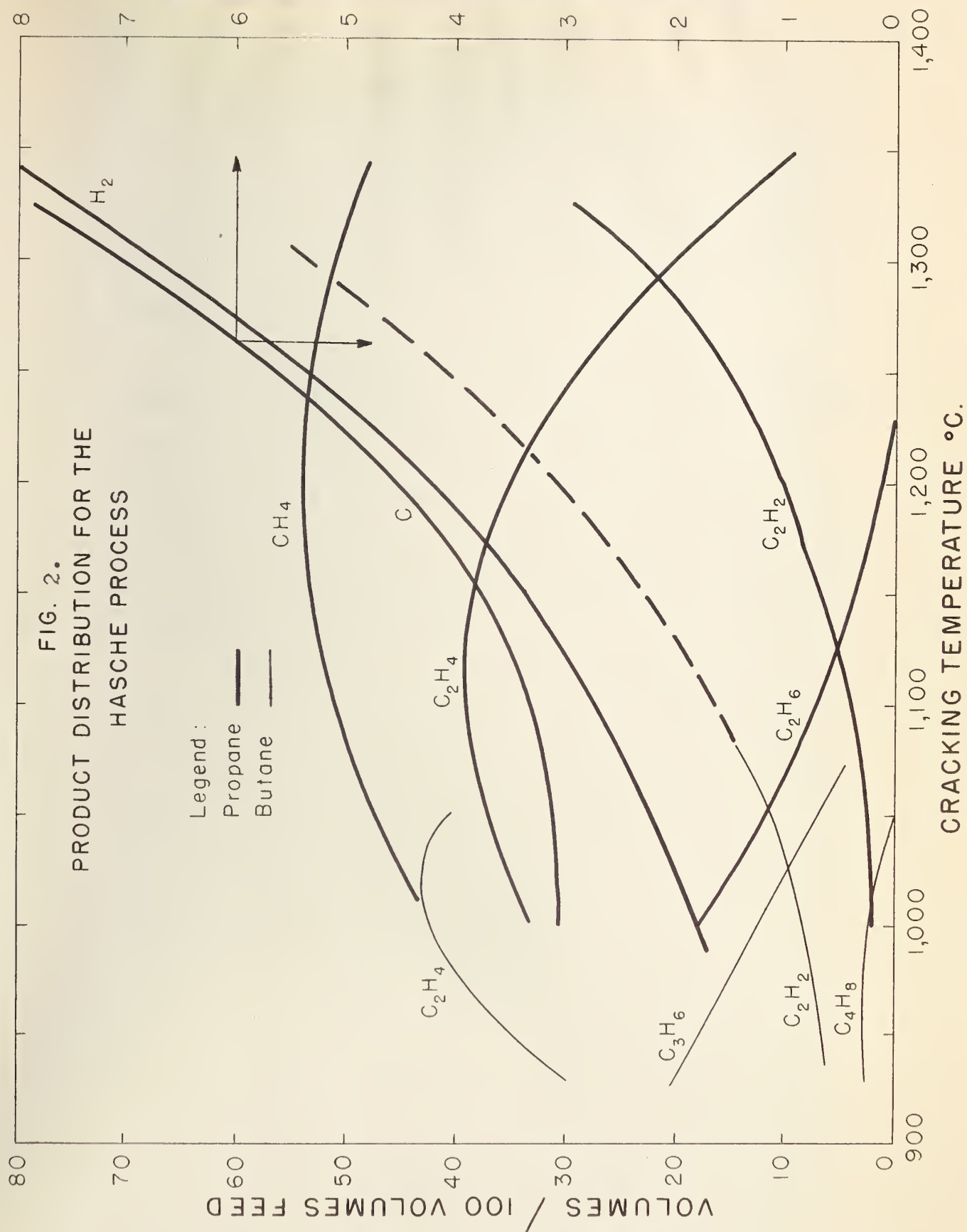
the products would be essentially all carbon and hydrogen.
Although the state of equilibrium was not approached, it
was felt that thermodynamic considerations would give an
indication of the nature of the reactions, and their
relative order. Free energy data was available from
Rossini (Fig. 3), and equilibrium products could be
computed. (21)

Preliminary study indicated that the only
products of import would be ethylene, acetylene, methane,
carbon and hydrogen. If it is assumed that all the
butane reacted to products, it may be shown that the
equilibrium ratio of acetylene-to-ethylene is a function
only of the temperature and of the partial pressure of
hydrogen in the ambient gas.

On the other hand, the equilibrium ratio of
acetylene-to-methane depends not only on temperature
and the partial pressure of hydrogen, but also on the
partial pressure of methane in the ambient gas.
Stoichiometric equations from which these ratios may be
calculated are represented below:

$$C_2H_4 \longrightarrow C_2H_2 + H_2 \quad \text{---- 1}$$

$$2CH_4 \longrightarrow C_2H_2 + 3H_2 \quad \text{--- 2}$$
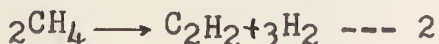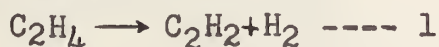
$$\frac{(C_2H_2)}{(C_2H_4)} = \frac{K_1}{(H_2)}$$

$$\frac{(C_2H_2)}{(CH_4)} = \frac{K_2 \, (CH_4)}{(H_2)^3}$$

The equilibrium ratios were calculated and

FIG. 3.
THERMODYNAMIC STABILITY OF HYDROCARBONS
AS RELATED TO FREE ENERGY OF FORMATION

Data of Rossini (21)
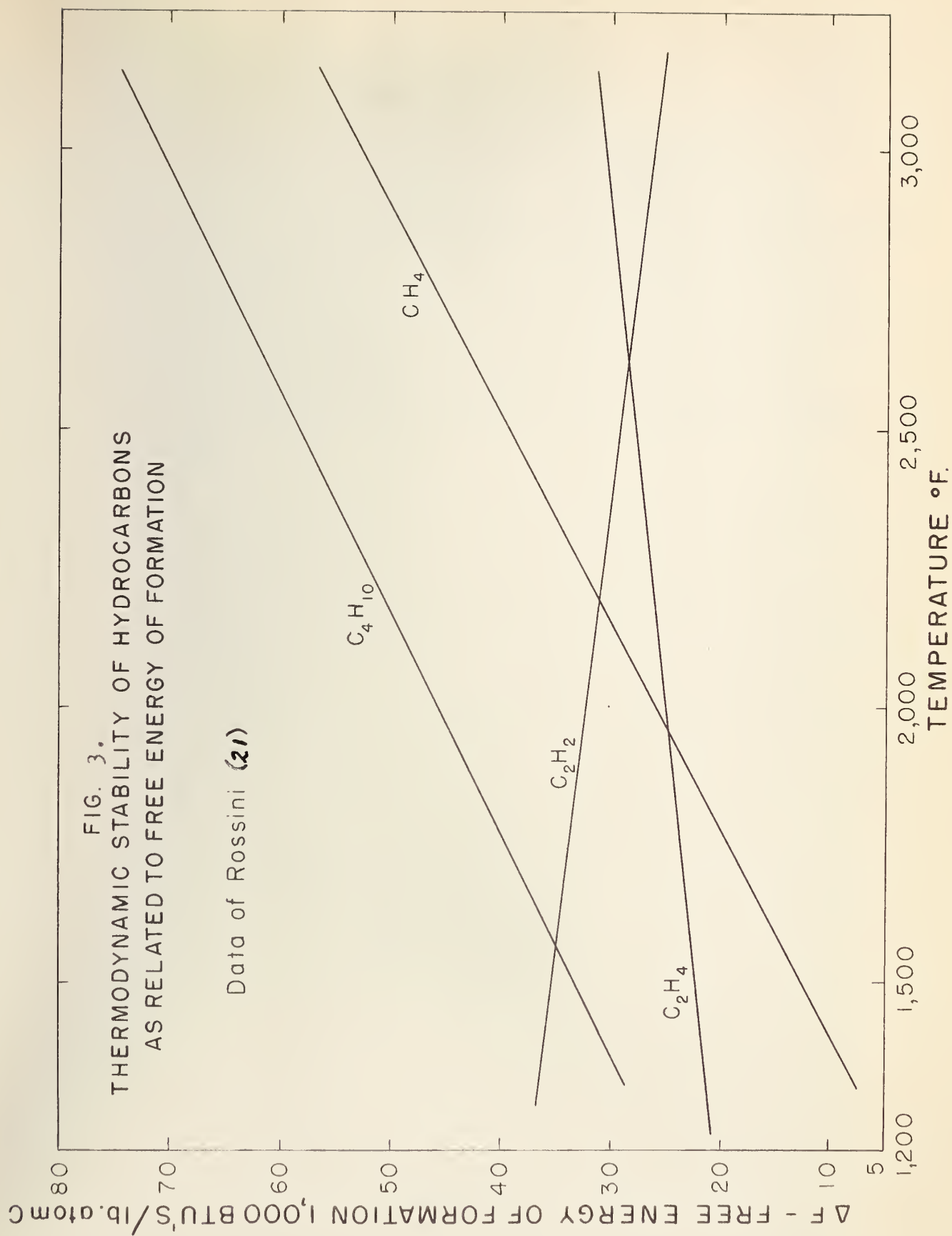
are shown in Figs. 4 and 5. Details of the calculations
are shown in Appendix A, Section f. and Table 7. A gas
temperature of 2400°F was selected for computation of
the acetylene-to-methane ratio. This temperature was
felt to be a good approximation after taking into consider-
ation the appearance of the acetylene-to-ethylene curve.
Heat transfer calculations shown in Appendix A, Section g.
indicate this value may be high, but even if an error
were introduced by this assumption, the general trends
are valid.

FIG. 4.
EQUILIBRIUM PRODUCT RATIOS
ACETYLENE TO ETHYLENE
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE

FIG. 5.

EQUILIBRIUM PRODUCT RATIOS

ACETYLENE TO METHANE
PYROLYSIS OF NORMAL BUTANE
AT   2400°F
IN THE PRESENCE OF METHANE
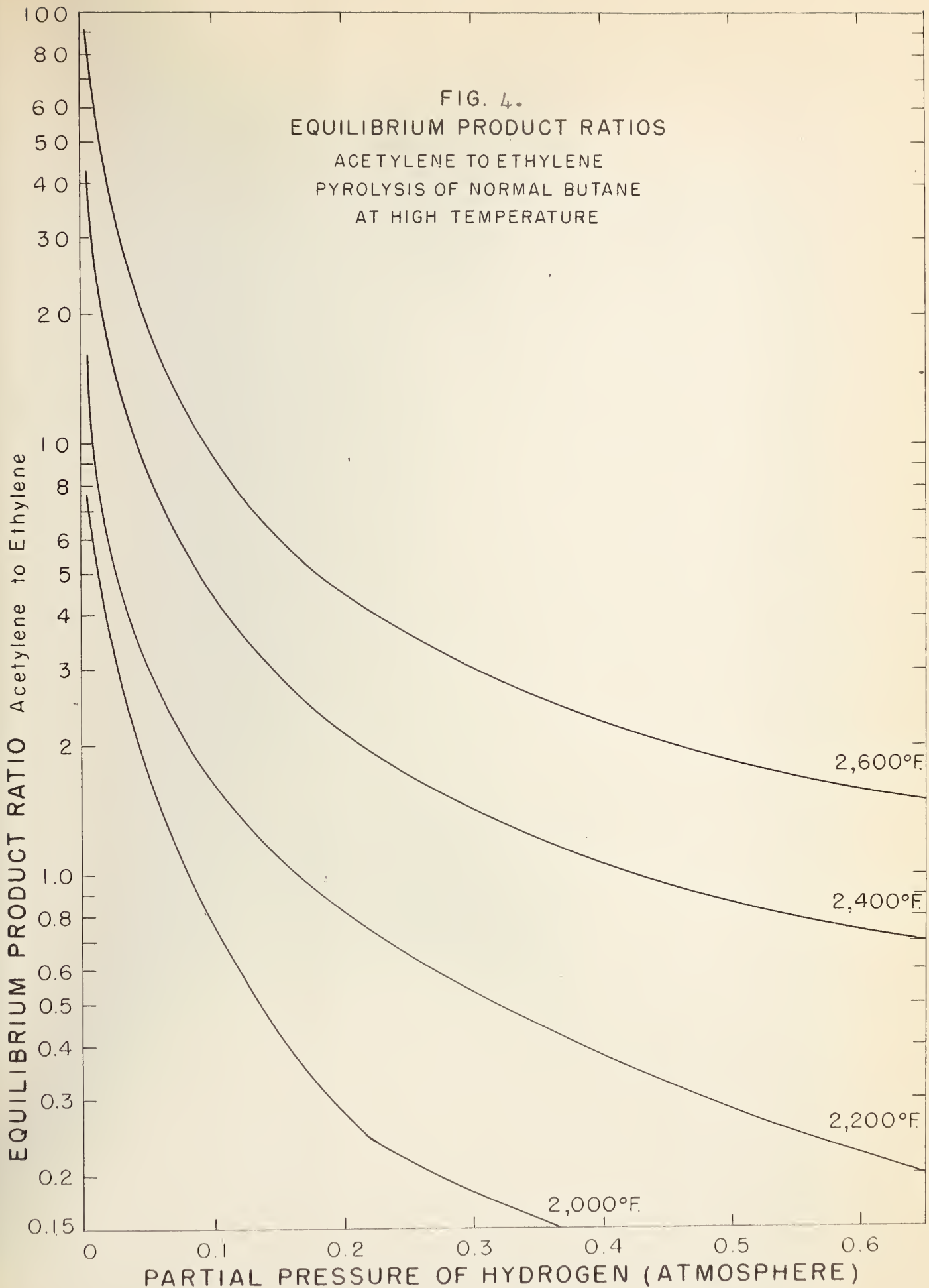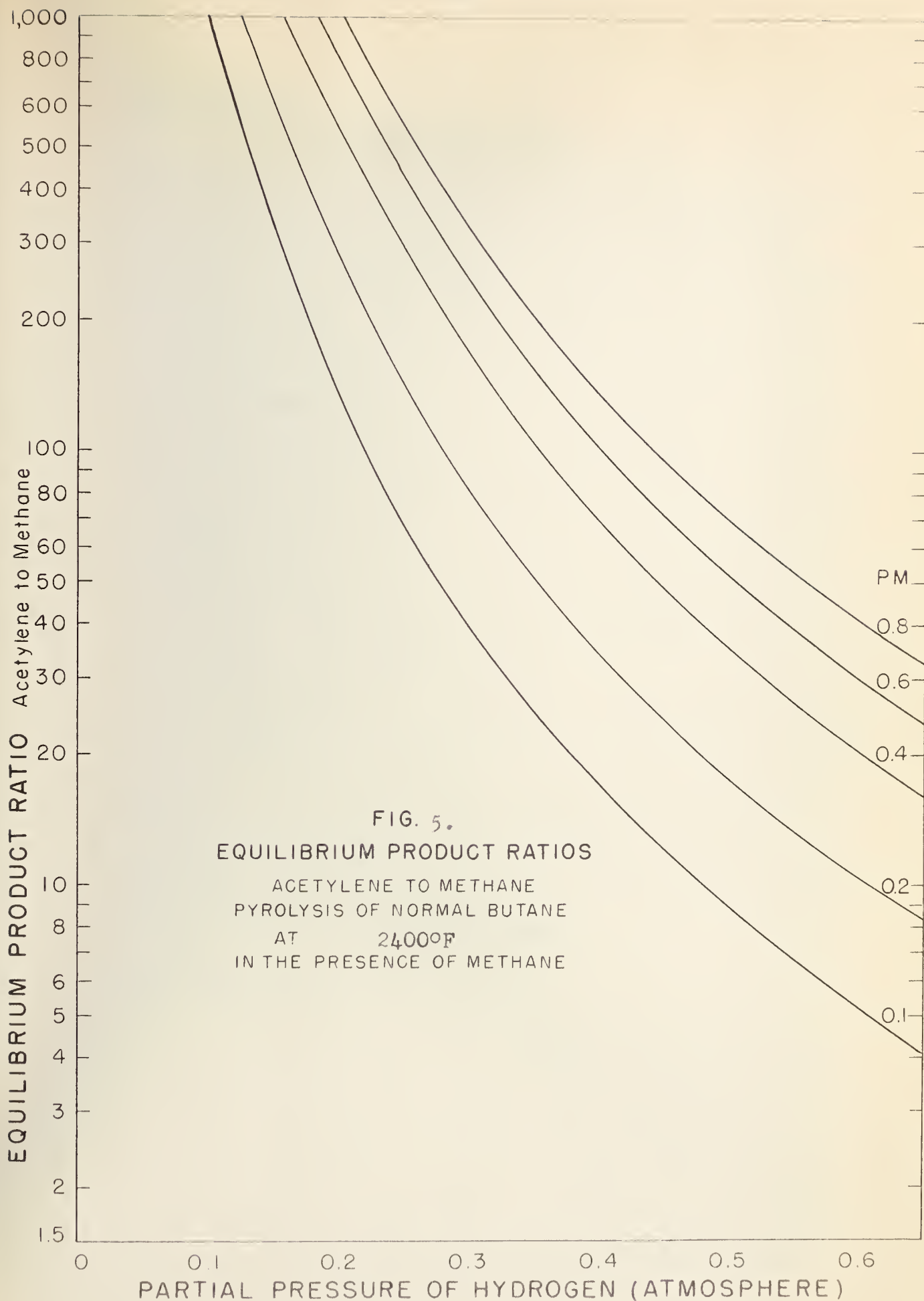
III Equipment:

The equipment used for this project was a modification of that in use for the carbon black project described elsewhere (19). Essentially the apparatus consisted of a furnace chamber in which a silicon carbide tube was located. The tube was connected by means of a neoprene hose to the feed gas system from which the desired mixture could be fed. The products of pyrolysis were passed through a glass cloth filter bag to remove carbon, and thence vented through an air ejector system. A schematic flow diagram is shown in Fig. 6. For descriptive purposes it is divided into three sections:

1. The reactor furnace and reactor tube.

2. The sampling system.

3. Means for measurement, control and services.

It was felt that only the first of these three components was unique to this application, and should be dealt with in detail. The others were thought to be important only inasmuch as certain features would affect the operation of the unit as a whole.

1.a. The Reactor Furnace

The reactor furnace occupied the second floor of the special equipment well in the new engineering building. The overall dimensions were approximately four feet in diameter by four feet high. The inside of the fire chamber was 24 inches in diameter and 30 inches high in the center, with the roof falling off domewise

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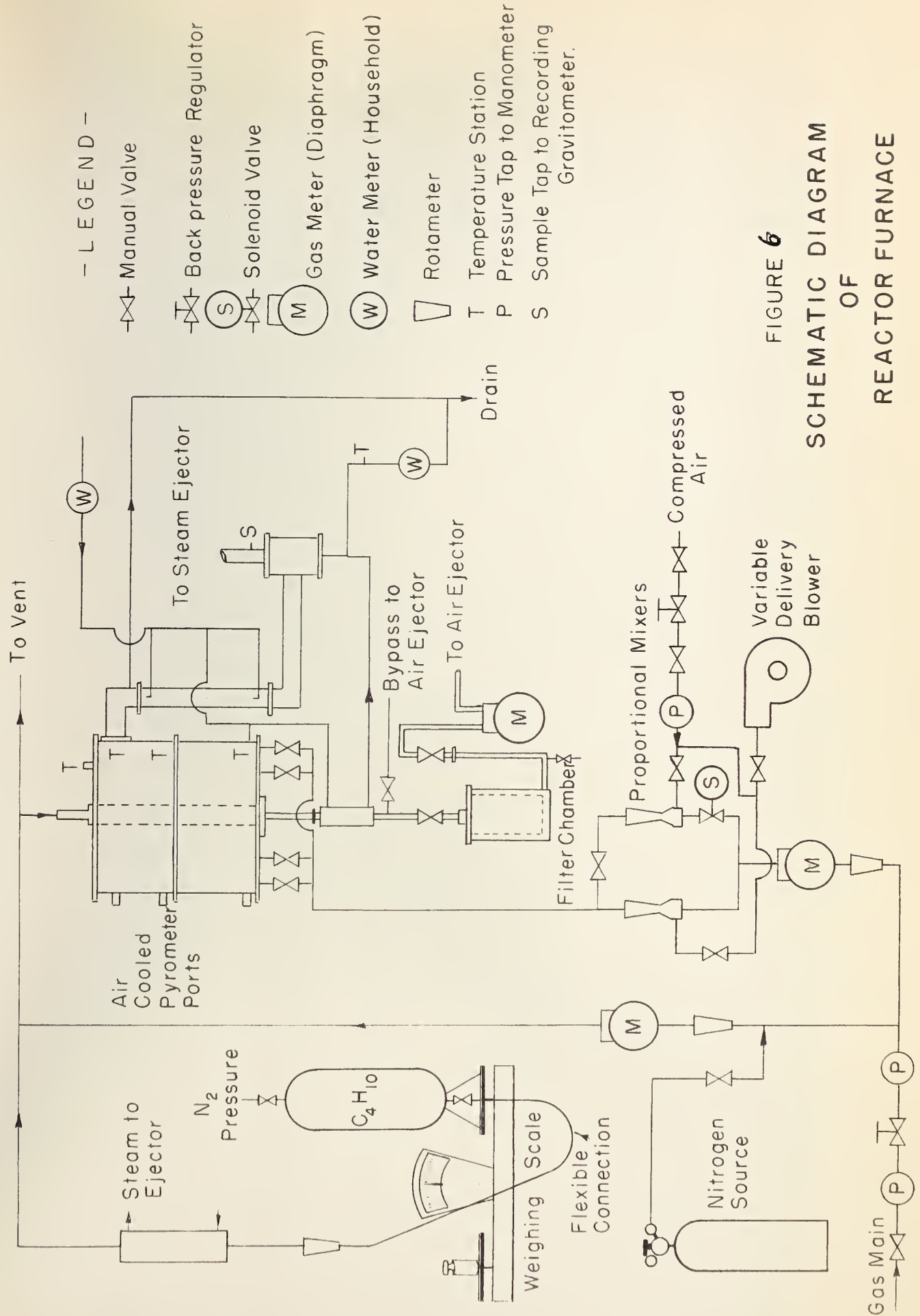
FIGURE 6

SCHEMATIC DIAGRAM
OF
REACTOR FURNACE

- LEGEND -

Manual Valve

Back pressure Regulator

Solenoid Valve

Gas Meter (Diaphragm)

Water Meter (Household)

Rotameter

T   Temperature Station

P   Pressure Tap to Manometer

S   Sample Tap to Recording
    Gravitometer.

to 24 inches at the outside edge. Heat was supplied by
the combustion of premixed natural gas and air supplied
to four McKee Wall Tight blast burners. Fig. 6a is a
photograph of the furnace body. The gas-air mixing was
accomplished with two Eclipse L.P. proportional mixers,
one of which was fitted for automatic control. The
capacity of the two mixers was balanced so that, by
intermittent operation of the smaller, the apparent
furnace temperature could be controlled at any point
within the range from about 2250°F, to 2500°F, to a
precision of perhaps 50°F. For higher temperature, the
furnace was operated at full thermal capacity.

The fire chamber was constructed in three
layers; fire brick, insulating fire brick and insulating
brick, and was jacketed by a water coil cooled mild
steel shell. The fire brick layer was constructed of
9 in. x 4½ in.x9 in. Kruzite cupola brick, followed
by 4½ in. of Castable Insulation No. 20, a vermiculite
cement, into which was embedded the cooling coil of
½ in. copper tubing. Details of the furnace construction
are presented in Fig. 7.

The base of the fire chamber consisted of
9 in. Kruzite fire brick on 3 in. Cast-O-Lite thermal
insulation. The roof of the chamber was formed of
plastic fire brick, overlain with Castable Insulation
No. 20. The shell was fabricated of mild steel plate;
½ in. base, ¼ in. top and 1/8 in. side plates.
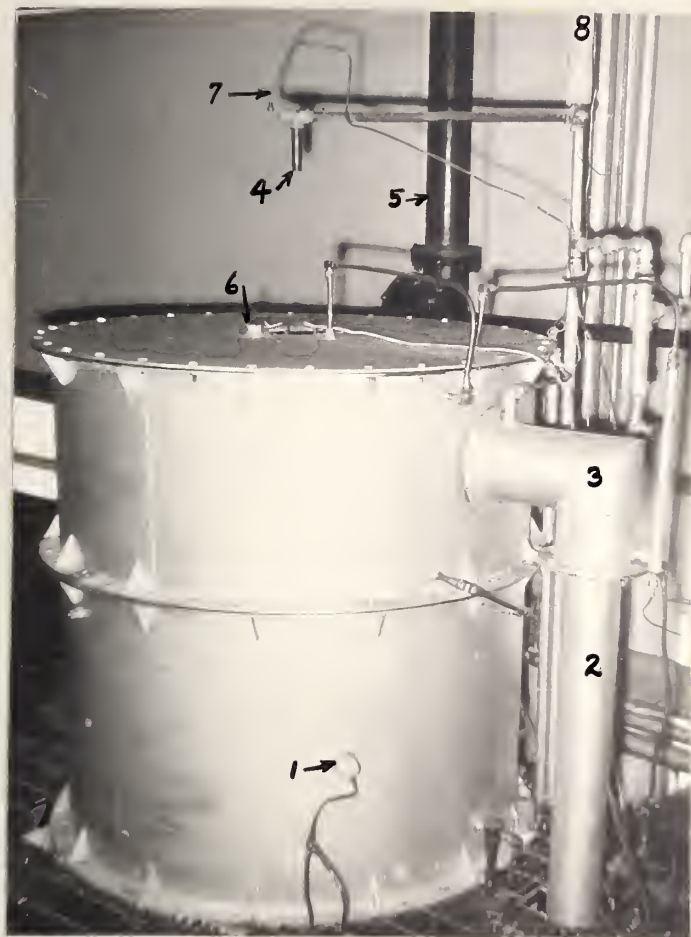
Fig. 6a   Reactor Furnace Body

1.   Lighting port with furnace pressure tap
                in place.
2.   Spray quench tower for flue gases.
3.   Jacketed stainless steel elbow.
4.   Reactor gas inlet.
5.   Gas vent system.
6.   Furnace wall thermocouple.
7.   Reactor tube pressure tap.
8.   Line to vent system.

FIGURE 7

CARBON BLACK
FURNACE ASSEMBLY

Scale $1\frac{1}{2}$ Inch = 1 Foot

Labels on figure: Plastic Firebrick, Tube Mounting, Thermocouple Mounting, Top Plate, Shell, Thin Split Kruzite, Flue Mounting, Cupola Blocks (Kruzite), Thermocouple Mountings, Insulation Brick, Kruzite Firebrick, Standard size, Costable Insulation, Pyrometer Port, Tap Out Block, Burner Port and Burner Mounting, Tube Mounting, Base Plate

-13-
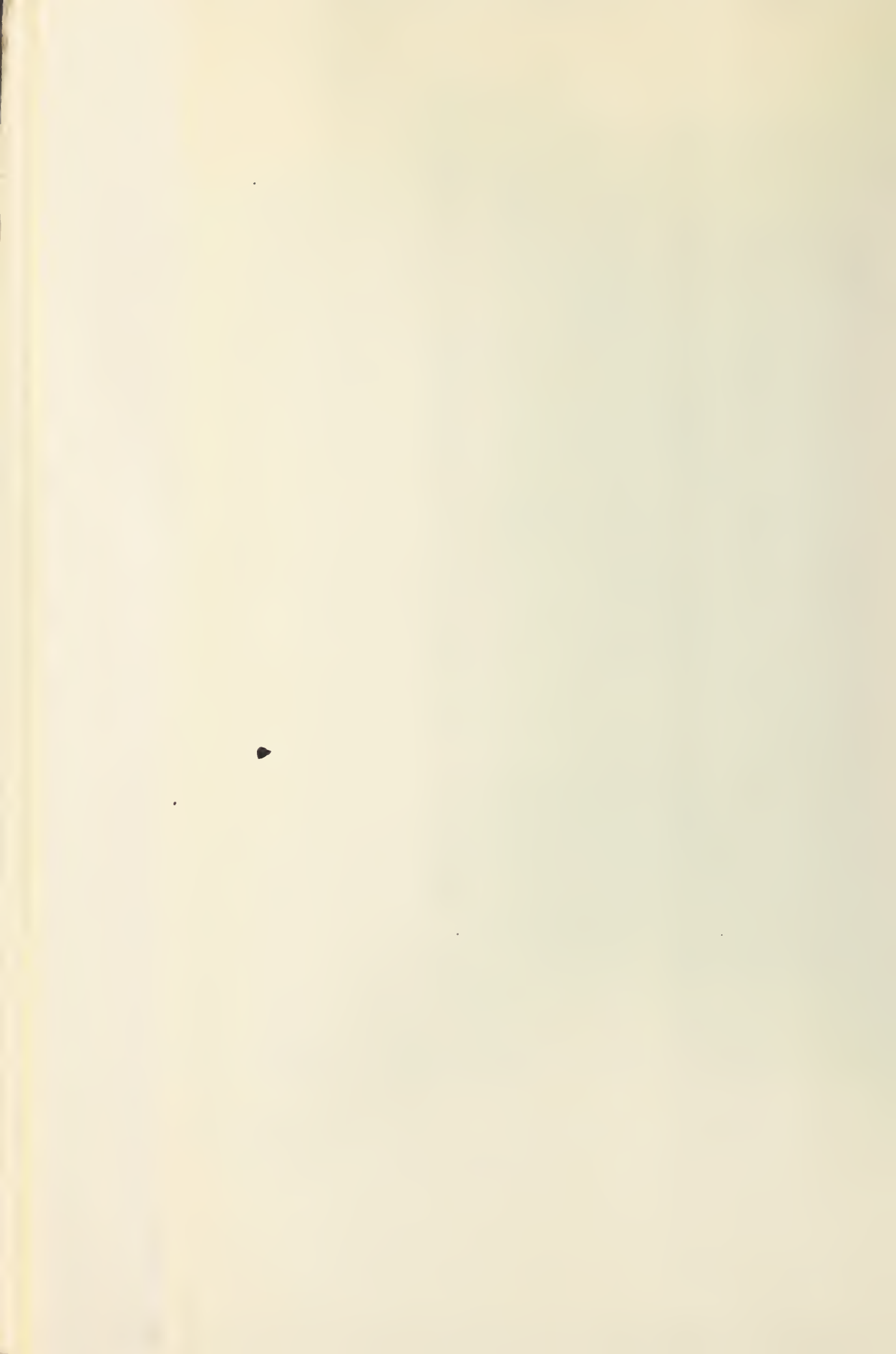
Provision was made for temperature measurement by means of both thermoelectric and optical means. Four platinum to platinum-10%-rhodium thermocouples were placed within the fire chamber wall to measure the furnace wall temperature as shown in Fig. 6a. Three pyrometer ports, supplied with air cooling, allowed an optical pyrometer to be focussed on the outside of the reactor tube.

The flue gases were removed radially from the top of the fire chamber by means of eight two inch alundum tubes, uniformly spaced around the periphery of the chamber. These tubes led into a 4 in. square cross-sectional duct that encircled the furnace. The flue gas duct was connected to the steel flue gas system by means of a 6 in. diameter alundum tube which projected into a water jacketed stainless steel elbow (Fig. 6a, part 3). The gases were then quenched by means of three water jets within a section of four inch pipe (Fig. 6a, part 2). The quench water was withdrawn to drain while the flue gases passed to vent. Pressure in the fire chamber was maintained at or near one atmosphere by means of a steam ejector.

b. The Reactor Tube

The reactor tube consisted of a 30 in. section of some type of ceramic, approximately 1 in. diameter. Two different types of tubes were used, alundum and

silicon carbide. The service demanded of these tubes was such that neither was found completely satisfactory, although each had advantages.

The main requirements of these substances could be summarized as follows:

(a) Sufficient mechanical strength for self support at elevated temperature, and to withstand high stresses introduced by the heavy thermal load over repeated heating and cooling cycle.

(b) Mechanical handling must be possible without special equipment.

(c) High thermal conductivity.

The above requirements were best met by the silicon carbide tube.

An alundum tube was found to satisfy (a), and (b) and could be mounted more readily than the silicon carbide, but developed blisters and fissures after several heating-cooling cycles. All the reported tests were carried out with the silicon carbide tube; the properties of which are as follows:

Inside Diameter ins.	Wall Thickness ins.	Thermal Conductivity $BTU/(hr.)(ft.)^2$ $(^oF)/in.$	Permeability at 2600^oF $scf/m.ft.^2hr.$ (in. of H_2O)	Tensile Strength at 2600^oF psi
1.125	3/8	109	0	1500

The reactor tube was mounted vertically in the center of the fire chamber, joined to a flanged base

using a cement composed of a paste of aluminum phosphate
and aluminum oxide. The aluminum phosphate was formed
by reacting a fine aluminum metal dust in about 100 cc.
of 85 percent phosphoric acid. This cement was recommended
by the manufacturers as the best high temperature cement
mix available.

The inlet to the tube was formed by cementing
a progressively smaller tube within the reactor tube,
until an outside diameter of 1 inch was reached. At
this stage it was simple to connect the reactor to the
feed gas system by means of a neoprene rubber hose.

It was found that frequent handling of the
reactor tube necessitated construction of a special base
plate. The plate incorporated a recessed opening, in
which the tubing could be butt cemented for tightness,
with a close fitting ring above this joint to provide
mechanical strength. When the entire recess was filled
with cement and cured in the proper manner, the impervious
seal was protected from mechanical strain by a collar of
cement surrounding the tube and fitting closely into the
recess. The mounting plates were assembled as shown in
Fig. 8; the completed assembly is shown in Fig. 8a.

2. Sampling and Product Recovery System

The carbon black produced during the reaction
was recovered by means of a filter (Fig. 9), a woven
glass fiber filter bag 8 in. diameter by 18 in. long.

$\frac{1}{2}"$ Plate 10" O.D. x 1 $\frac{7}{8}"$ I.D. hole to fit Ceramic tube.

8 Bolt holes on 8" dia. centre to fit $\frac{5}{8}"$ bolts

4 Holes tap $\frac{3}{8}"$ thread on 4"dia. centre.

Ceramic tube 1 $\frac{7}{8}"$ O.D. x 1 $\frac{1}{8}"$ I.D. x $\frac{3}{8}"$ Wall

Tube; cement here.

Recessed Flange, and 2"Coupling welded on Flange.
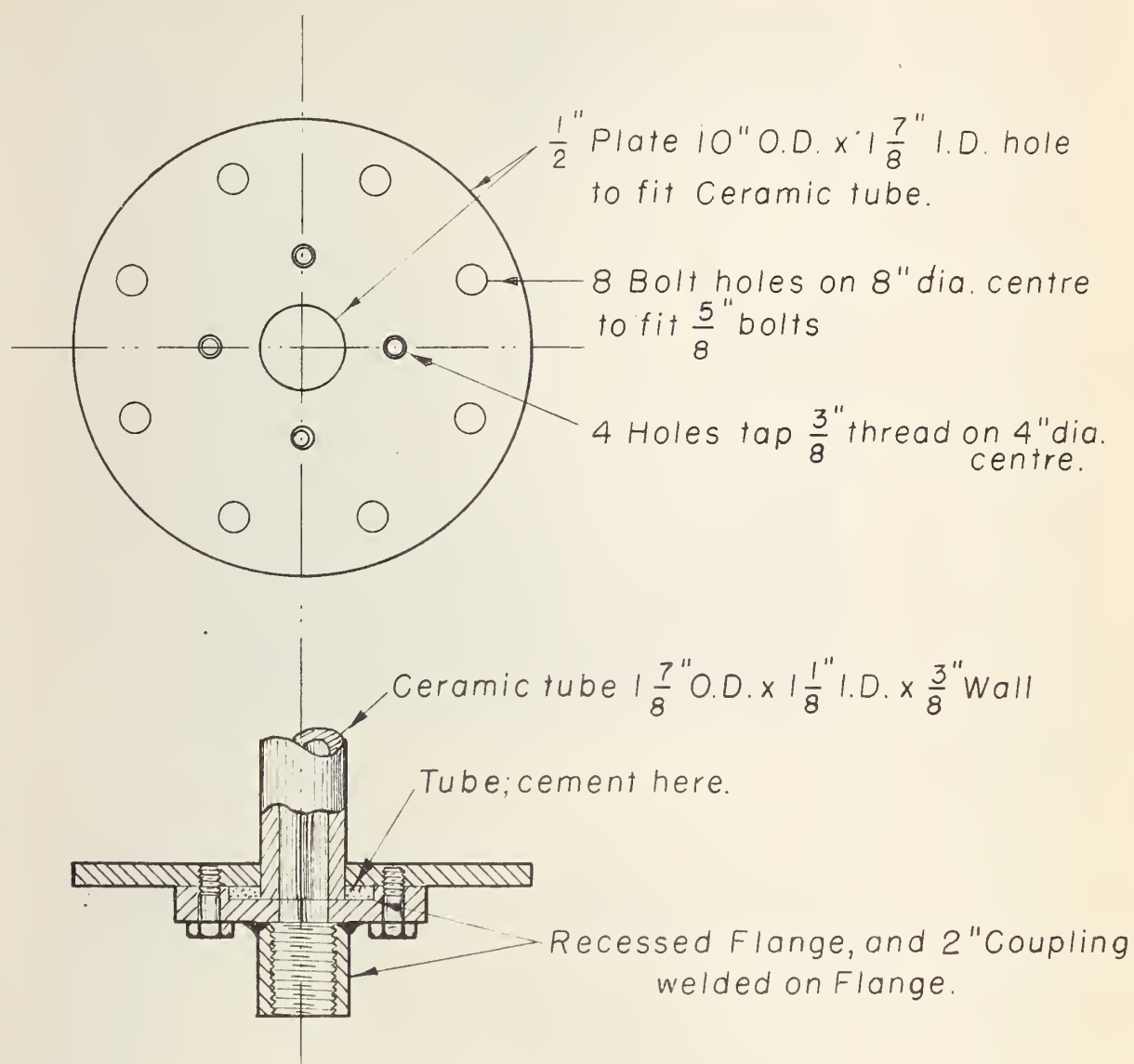
FIGURE 8.

MOUNTING PLATE AND FLANGE FOR PYROLYSIS TUBE

Pyrolysis of Normal Butane at High Temperature.

Fig. 8a Reactor Tube and Mounting Assembly

—8" O.D. STEEL RING

GLASS CLOTH
FILTER BAG
8"Dia. x18"L.

STANDARD 2"COUPLING

1"PIPE

$\frac{1}{4}$" S.S.VALVE

24"

10"
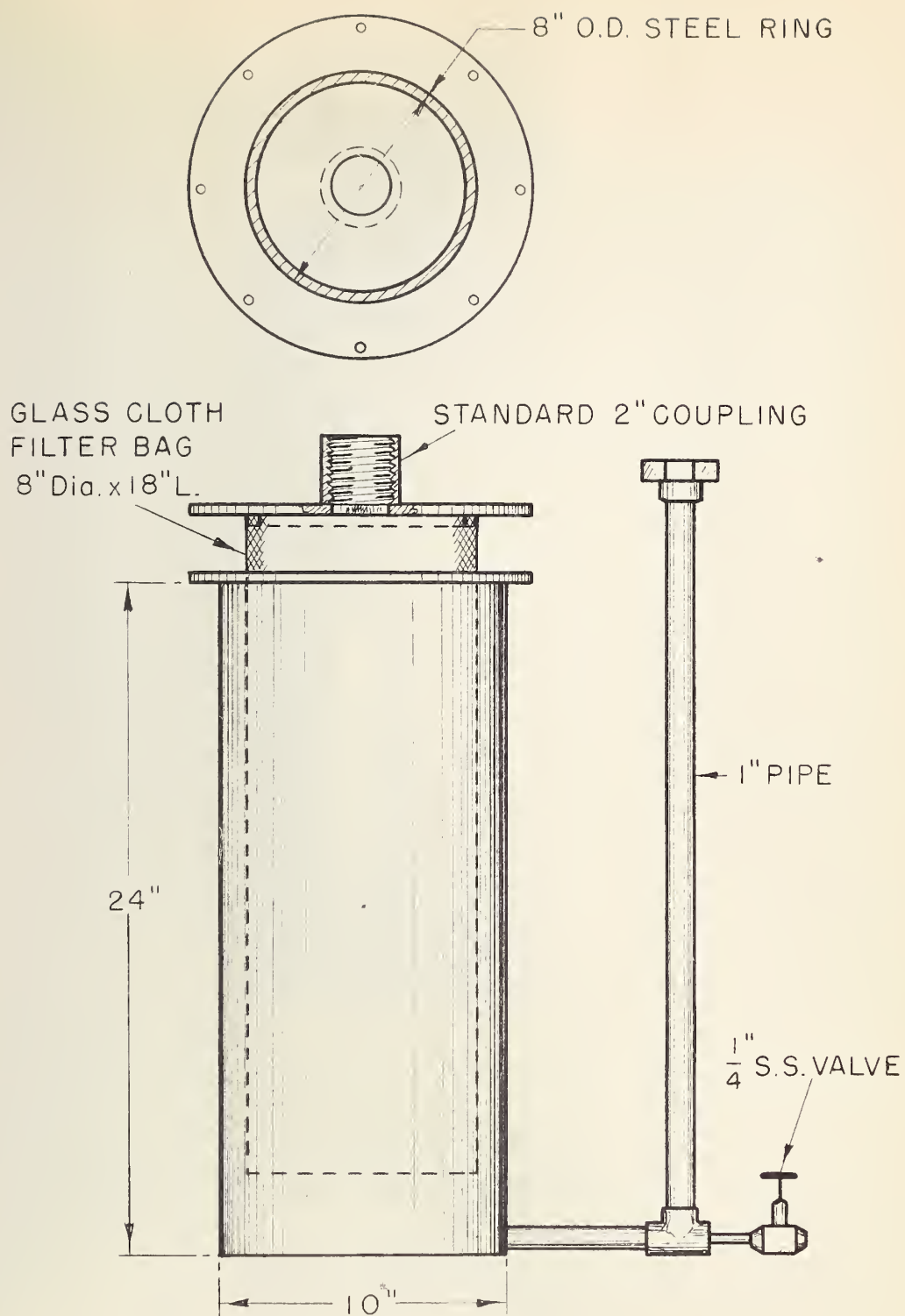
FIG. 9.

CARBON BLACK FILTER, FOR PYROLYSIS OF
BUTANE AT HIGH TEMPERATURE

Fig. 9a   Filter Chamber Assembly

1.   Filter chamber.
2.   Quench cobler jacket.
3.   Off gas line.

The black was collected on the inside of the bag, and could be measured by weighing.

The filter chamber consisted of a cylindrical mild steel vessel (Fig. 9a, part 1), connected to the reactor tube by means of a 2 in. pipe (Fig. 9a, part 2), and to the off-gas system by a 1 in. line as shown in Fig. 6 and Fig. 9a, part 3. The carbon black was removed in the filter bag to be weighed for carbon recovery. Gaseous products from the system passed through a cooled section of pipe (Fig. 9a;2), between the furnace and the filter chamber to remove excessive heat from the gases and stop the reactions.

Gas sampling was accomplished by means of a small diaphragm type pump (Fig. 10, part 3). The gas was collected by water displacement from suitable containers, e.g. sample bulbs or stoppered flasks (Fig. 10, parts 2 and 5), to be analysed by orsat analyser. A simultaneous sample was taken by a special sampler for acetylene determination by precipitation from silver nitrate (Fig. 10, part 1). Samples for Podbielniak analysis were taken into evacuated containers of approximately 1 cubic foot capacity.

3. Measurement, Control and Service Supply

The instrumentation has been shown symbolically on the flow diagram (Fig. 6). Gas metering was accomplished by means of bellows type domestic meters, water
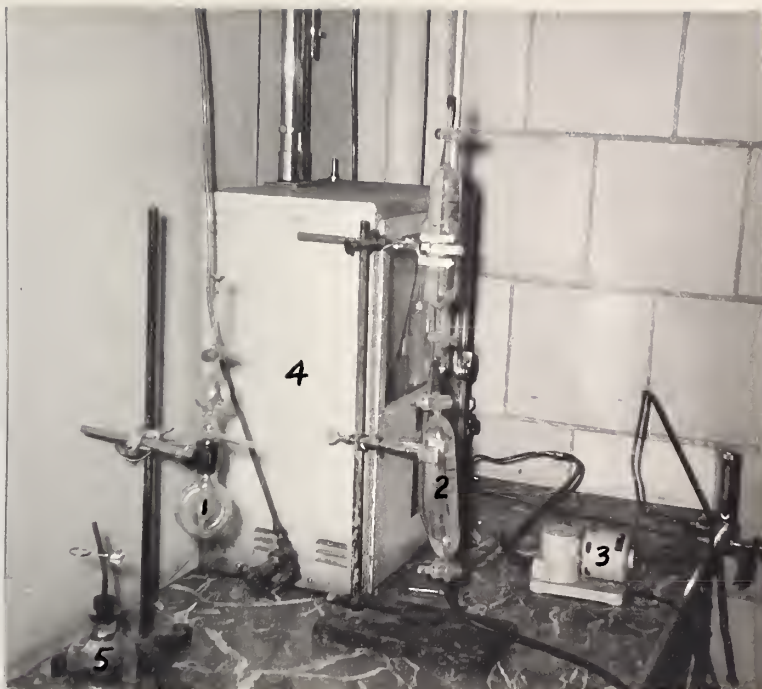
Fig. 10   Gas Sampling System

    1.   Acetylene sampler.
    2.   Sample containers.
    3.   Diaphragm type sampler pump.
    4.   Recording gas gravitometer.
    5.   Water displacement sample container.
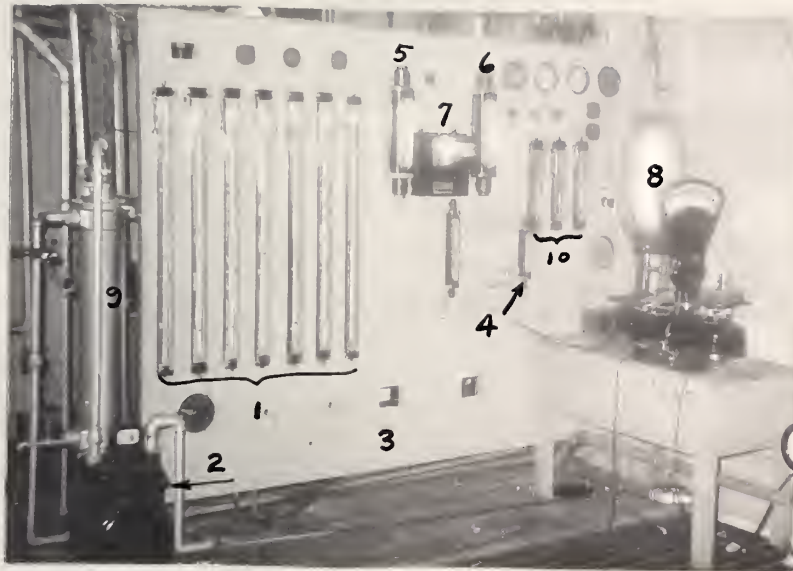
Fig. 11   A front view of the instrument panel,
          showing observation points for various data

          1. Manometers to various points in the system.
          2. Off gas meter.
          3. Diluent gas meter.
   4, 5, 6. Rotameters for butane, reactor gas, fuel gas.
          7. Brown pyrometer controller (not in use).
          8. Butane supply cylinder.
          9. Off gas cooler.
         10. Service control rate manometers.

metering by household type water meters. Small pressure differentials were measured by means of water manometers (Fig. 11, part 1), the larger differentials by means of war surplus air speed gauges. Rotameters were used to show rates of flow in both gas and liquid systems (Fig. 11, parts 4, 5 and 6). The panel board arrangement is shown in Fig. 11.

Furnace temperatures were measured by means of platinum-platinum rhodium thermocouples; apparent reaction temperature (pyrolysis tube temperature) by means of a Leeds-Northrup hot wire type optical pyrometer. Metering temperatures were taken as room temperature or measured using a contact pyrometer.

Combustion air was supplied from a Roots-Connersville rotary type positive blower, size 44, with a capacity of 90 c.f.m. against 1 p.s.i.g. The air-gas mix was accomplished by means of two Eclipse Series L.P. air-gas proportional mixers, Cat. No. 44-L.P. and 64-L.P., with a total natural gas capacity of about 8 cfm. against 1 p.s.i.g.

Steam and compressed air supplied to the furnace were obtained from the University Power Plant with the exception of the combustion air as above.

A means of temperature control for the furnace was provided using a Brown indicating electric pyrometer, (Fig. 11, part 7). The pyrometer activated a solenoid

valve to the gas inlet of the smaller proportional mixer. During these tests, temperature control was not practical because of excessive heat load, and the furnace was operated at full thermal capacity.

IV Feed Stock

The butane used in this investigation was commercial grade normal butane supplied by Imperial Oil Ltd., Calgary Refinery. The gas analysed approximately $8\frac{1}{2}$ percent isobutane by Podbielniak analysis. (This analysis was qualitatively confirmed by gas phase chromatographic technique.)[*]

The nitrogen used for dilution purposes was a purified grade obtained from a local firm. The gas has been tested to as low as 0.1 percent oxygen, and has been known to contain as much as 0.5 percent oxygen.

Natural gas was taken directly from the city gas mains, measured approximately 1000 B.T.U./cf. heating value. A carbon number of 1.04 was found by analysis. The gas contained 10 percent air.

[*]This test was made by Dr. A. Blades, Research Council of Alberta.

V Procedure:

       In order to obtain the best possible control of the variables under investigation, the following general experimental procedure was adopted.

       a. The reactor was flushed with nitrogen to purge the air.

       b. A bypass (Fig. 6a, part 8) was opened to vent the gas flow.

       c. Reactor gas rates were adjusted, natural gas and nitrogen by the calibrated rotameter (Fig. 11, part 5), butane by weight difference from the reservoir (Fig. 11, part 8) with the aid of the butane rotameter (Fig. 11, part 4).

       d. The experiment was started by switching the reactor gas flow from the vent to the reactor tube inlet (Fig. 11, part 8 to part 4). At this time, all initial readings of meters, temperatures and pressures were taken and a timer started. As the run progressed, the behavior of the equipment was closely observed to allow the longest possible time lapse before beginning to sample. When the pressure drop across the reactor tube became large and erratic, the samples were stopped, and the reactor gases were turned to vent. The feed gas system was flushed with nitrogen, then the reactor tube was again purged. After the nitrogen purge, a small stream of air was passed through the reactor tube to remove carbon deposits.

       e. Acetylene in the product gases was analysed

by precipitation as a silver salt. The acid evolved was back titrated with standard base (1).

f. The filter bag, containing carbon black from the reaction was removed and weighed to determine the amount of carbon formed.

VI Experimental Data:

The data for these pyrolyses were gathered under conditions of incomplete control; the accuracy of the chosen variables, temperature, space velocity and dilution with a non-reacting gas[*] were limited by the following factors:

1. The best available means for measurement of temperature at this level, the optical pyrometer, determined the temperature of the outside of the reactor tube. The measuring instrument was capable of a precision in the order of $10^{\circ}F$, and, as applied, was thought to have an absolute accuracy in the order of $50^{\circ}F$. The temperature of the outside surface of the reactor tube was determined, and the data recorded as observed at that temperature. During the course of a set of experimental work, this recorded temperature changed by as much as $100^{\circ}F$. It was felt that the gas temperature in the reactor lagged the apparent temperature by an amount dependent on the thermal demand on the tube; this in turn was roughly proportional to the quantity of butane in the feed. Computations show that a temperature drop of $100^{\circ}F$ through the tube wall was not unreasonable. (Appendix A, Section g.) The true pyrolysis temperature, was thought to be an average of a declining quantity, related somehow to the feed composition. A good approximation of the temperature of pyrolysis was thought to be about $200^{\circ}F$ below the

[*]The products of decomposition of natural gas were subtracted from the total decomposition gases to examine the effects of dilution alone.

recorded value. In the majority of the data reported this approximated 2400°F.

Since the time required to obtain a satisfactory gas sample was in the order of $1\frac{1}{2}$ to 2 minutes, and the length of the experimental period was seldom greater than 5 minutes, it was necessary to begin sampling after about 3 minutes of experimentation. At this time, the conditions in the reactor tube were known to be in unsteady state. Near the end of each run, it was noted that the rate of apparent temperature change was much less. It was felt that at these temperature and heat load conditions, steady state could be established in about 6 minutes.

2. Any inaccuracies in analysis were greatly magnified by the large quantities of inert material present. A reasonable balance was obtained for both carbon and hydrogen when the appropriate metering factors were applied to these analyses, and they were adjusted to a nitrogen balance (Appendix A, Table 1), but it was thought that some of the scattering among the data was due to analytical error.

3. The dilution gas influenced the decomposition by helping to establish thermal equilibrium within the reactor tube. The furnace was operated at maximum capacity, and the temperature was maintained as high as possible under the heat load conditions. When the diluent gas was transparent to radiation,

the main heat load was absorbed by the reacting butane.
Changes in butane concentration resulted in relatively
large variations in heat load, and the pyrolysis temper-
ature changed accordingly. When natural gas was used
as a dilution agent, the methane received radiation, and
the heat load was considerably less dependent on butane
concentration. This point was illustrated by the fact
that there was a considerable decrease in the uncertainty
of data when natural gas high in methane was used as the
dilution agent. The extent of decomposition of butane
to carbon and hydrogen decreased markedly.

In order to establish the best interpretation
of the data, cognizance was taken of temperature drift,
deviation in space velocity and internal deviations in
the curves. The lines drawn were thought to be more
meaningful than "best fit" curves. From studies in the
available literature concerning high temperature pyrolysis
of hydrocarbons and preliminary tests, it was decided
that the main products of pyrolysis at the conditions
under investigation were acetylene, ethylene, hydrogen,
carbon and methane. Analytical work was based on this
assumption, and occasional tests were made to determine
whether the assumptions were sound. Only minor quan-
tities of other constituents were detected during these
tests. Sample calculations of the balances, yields,
equilibrium concentrations and product ratios, together
with tabular summaries of these quantities are presented
in Appendix A, Sections a, b, c, d and e, and Tables 1 to 6.

A. Pyrolysis with Nitrogen Dilution

The products of pyrolysis in the presence of large quantities of nitrogen were determined at three space velocities, 25, 35 and 45 sec.$^{-1}$. Temperature was held as constant as the varied heat load conditions would permit, and the partial pressure of butane in the feed gas was varied.

Fig. 12a, 12b, and 12c show the product distribution per 100 moles of butane feed on the basis of partial pressure of butane in the feed gas, (Appendix A, Table 2.).

The commercially saleable products, acetylene and ethylene are both seen to be produced in large yields, the relative yields being greatly influenced by partial pressure. At the three space velocities*investigated, acetylene yields were increased to about 35 to 45 moles per 100 moles butane in the feed gas at 0.1 atmospheres partial pressure, while ethylene appeared to be favored by higher concentrations. At 0.1 atmosphere, 45, 60 and 80 moles of ethylene per 100 moles of butane in the feed were present, at space velocities of 25, 35 and 45 sec.$^{-1}$ respectively, while at 0.5 atmospheres and 25 sec.$^{-1}$, 80 moles per 100 moles of butane feed were formed. At the higher space velocities, the ethylene yield was noted to drop off above 0.4 atmospheres. This was thought to be due to incomplete conversion effects (of butane).

Methane and hydrogen were produced in large

* Space velocity was defined as the volumetric rate of flow per unit reactor volume.

quantities (approximately 200 moles), hydrogen as an additional product during the decomposition of butane to the products carbon, acetylene and ethylene. Methane represented either the decomposition of butane to methane and propylene, or further decomposition of the ethylene molecule. Methane was produced more readily at high butane concentrations.

The carbon yield was shown only on Fig. 12a, since it remained relatively constant. The production of carbon during each of the various tests was relatively insensitive to partial pressure. To establish internal consistency among the curves, the yield was taken to be constant at each space velocity. The order of magnitude was found to be 90, 80 and 70 moles/at space velocities 100moles of butane feed of 25, 35 and 45 sec.$^{-1}$ respectively based on the apparent temperature of the reactor gas.

The extent of butane decomposition during these tests was a complex variable, depending on many factors, including temperature, space velocity, and partial pressure. Since it was not possible to control this variable closely, it was felt that the decomposition data could better be presented on the basis of some internal parameter of the system.

Accordingly, Figs. 13a, 13b and 13c were prepared from the same data (Appendix A, Table 2) on the basis of butane reacted. The butane remaining in the product gases was considered as an "inert" diluent. On
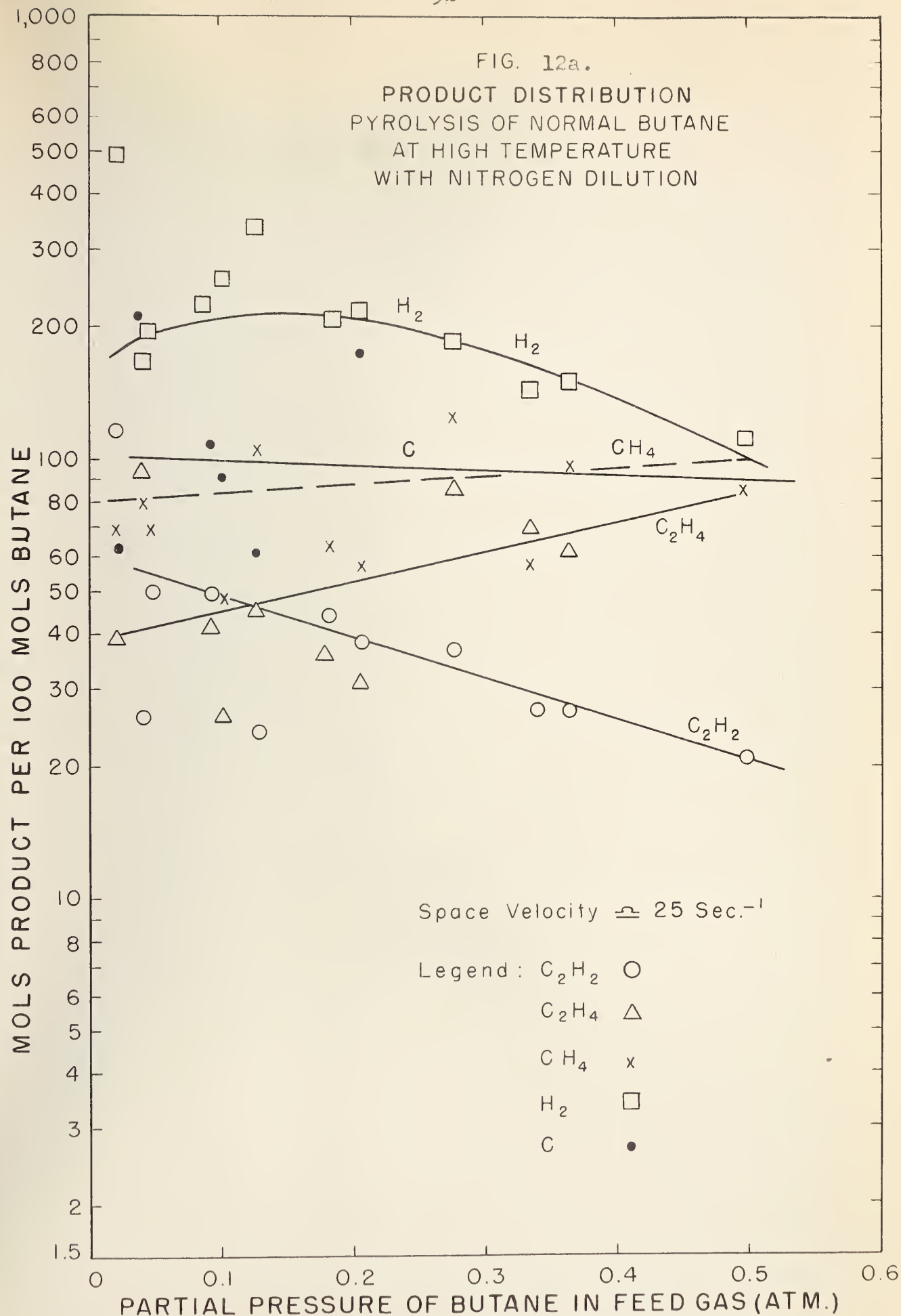
FIG. 12a.
PRODUCT DISTRIBUTION
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NITROGEN DILUTION

Space Velocity ≏ 25 Sec.⁻¹

Legend: C_2H_2 ○
C_2H_4 △
CH_4 ×
H_2 □
C ●

MOLS PRODUCT PER 100 MOLS BUTANE

PARTIAL PRESSURE OF BUTANE IN FEED GAS (ATM.)

FIG. 12b.
PRODUCT DISTRIBUTION
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NITROGEN DILUTION

FIG. 12c.
PRODUCT DISTRIBUTION
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NITROGEN DILUTION
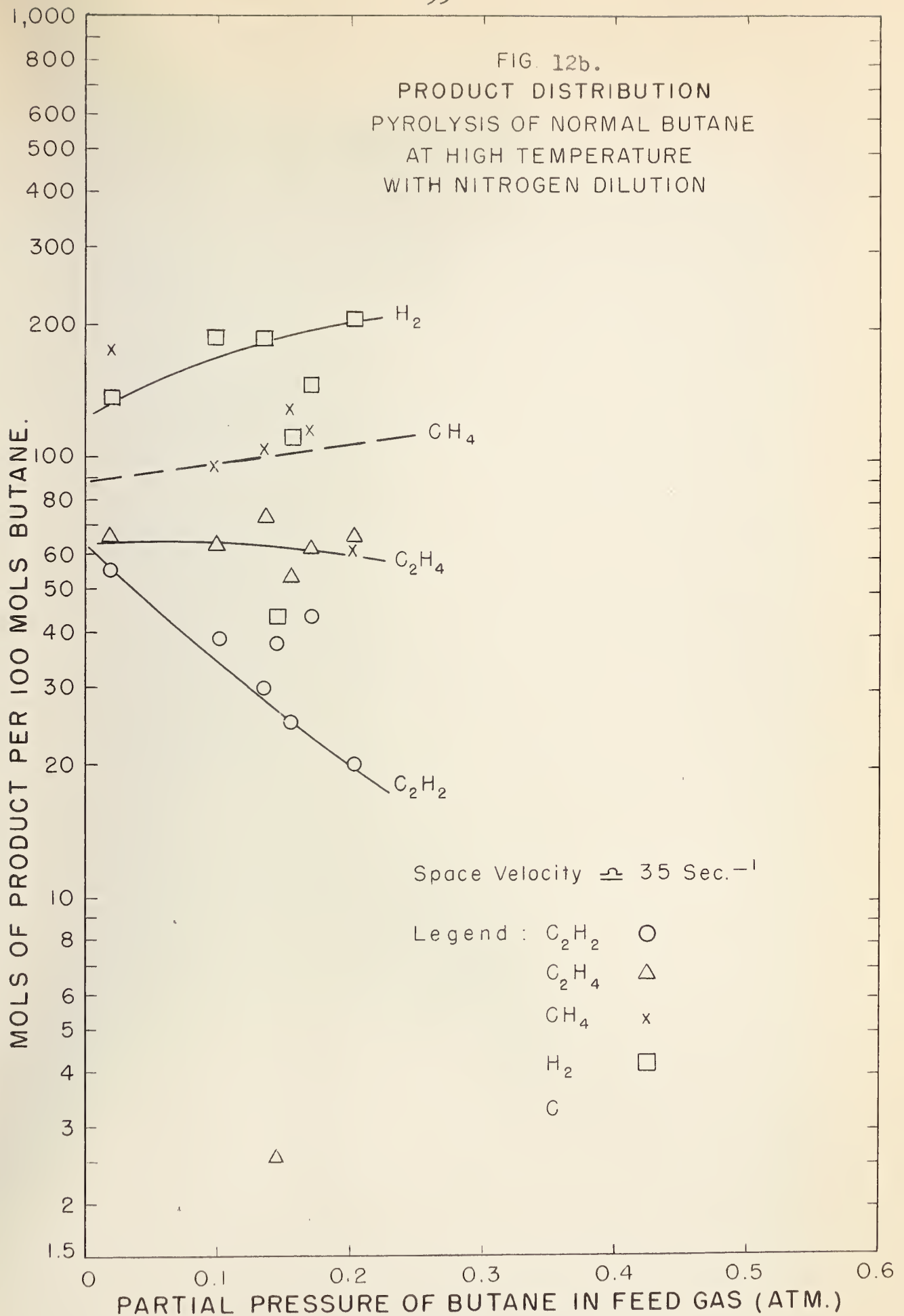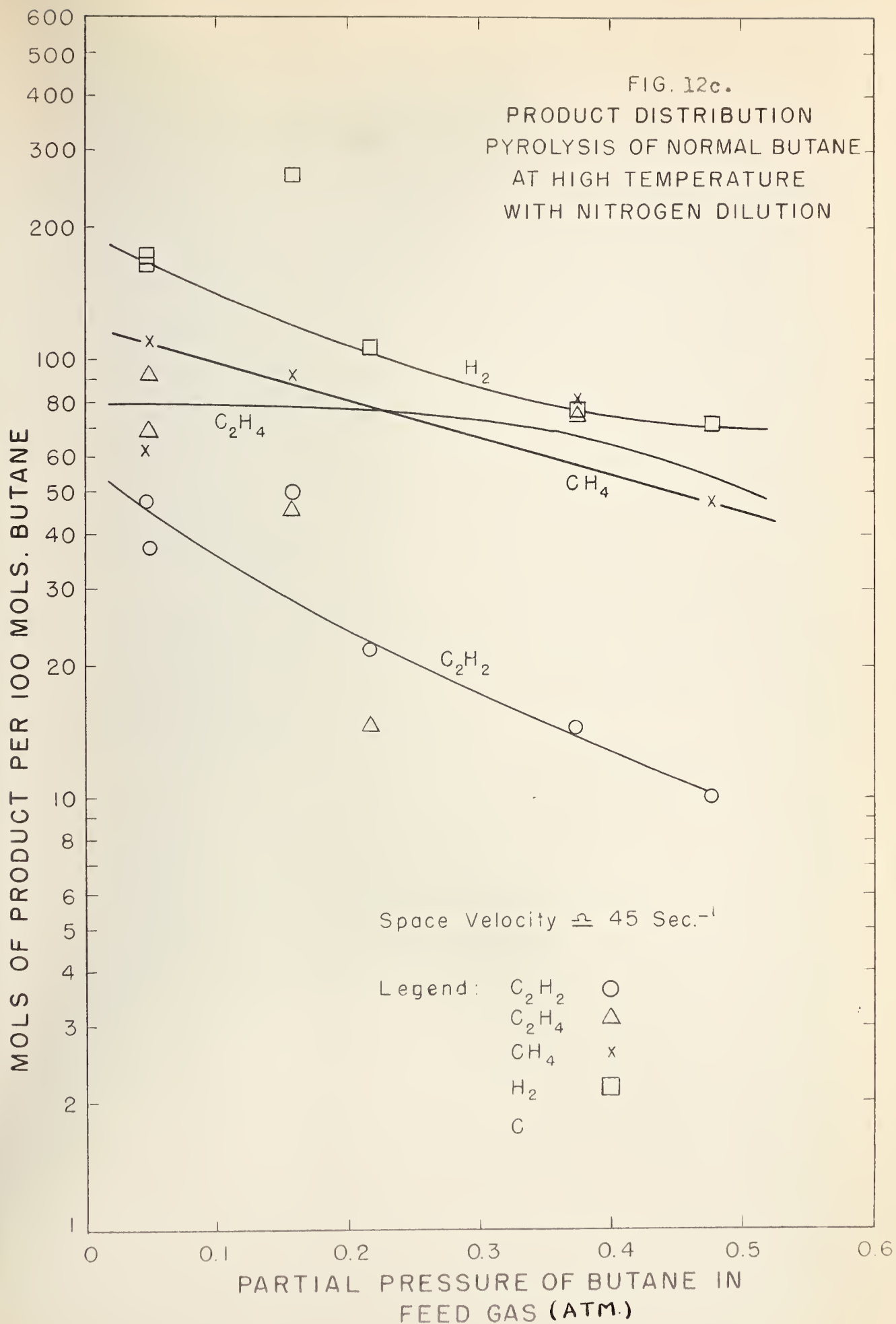
this basis, the formation of acetylene and ethylene appear to be complementary with a total yield of approximately 90 to 100 moles. Acetylene was more readily formed at low concentrations (a yield of about 50 moles per 100 moles of butane was noted at 0.1 atmosphere). Formation of ethylene at very low concentration was apparently favored most at some intermediate space velocity between 25 and 45 sec.$^{-1}$. The crossover point at which acetylene becomes more readily favored than ethylene is at a progressively lower partial pressure of reactant as the space velocity increases, at a yield of about 40 moles per 100 moles of butane.

The production of methane and hydrogen were apparently fostered by low reagent concentration. The inversion of the trend at 35 sec.$^{-1}$ was thought to be due to analytical uncertainty.

B. Pyrolysis in the Presence of Natural Gas

From a practical viewpoint the pyrolysis of butane in the presence of nitrogen offers some difficulties; nitrogen supply and product separation would add considerable cost to the operation. One solution to these problems would be to use a more readily separable diluent, such as steam, or pyrolyse the butane in its natural state, i.e. in a stream of natural gas. The pyrolysis of normal butane in the presence of natural gas was studied at a space velocity of 30 sec.$^{-1}$ and varied dilution ratios.

FIG.13a.
PRODUCT DISTRIBUTION
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NITROGEN DILUTION

Space Velocity $\simeq$ 25 Sec.$^{-1}$

Legend: C_2H_2 O
         C_2H_4 $\triangle$
         CH_4 x
         H_2 □

H_2

CH_4

C_2H_4

C_2H_2

MOLS OF PRODUCT PER 100 MOLS REACTANT BUTANE

PARTIAL PRESSURE OF REACTANT IN FEED (ATM.)

FIG 13b.
PRODUCT DISTRIBUTION
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NITROGEN DILUTION

Space Velocity $\simeq$ 35 Sec.$^{-1}$

Legend: C_2H_2 O
         C_2H_4 $\triangle$
         CH_4 x
         H_2 $\square$

Assume a constant product of
80 mols Carbon

MOLS PER 100 MOLS REACTANT BUTANE

PARTIAL PRESSURE OF REACTANT IN FEED (ATM.)

FIG. 13c.
PRODUCT DISTRIBUTION
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NITROGEN DILUTION

Space Velocity ≅ 45 Sec.

Legend : C_2H_2 ○
          C_2H_4 △
          CH_4 x
          H_2 □
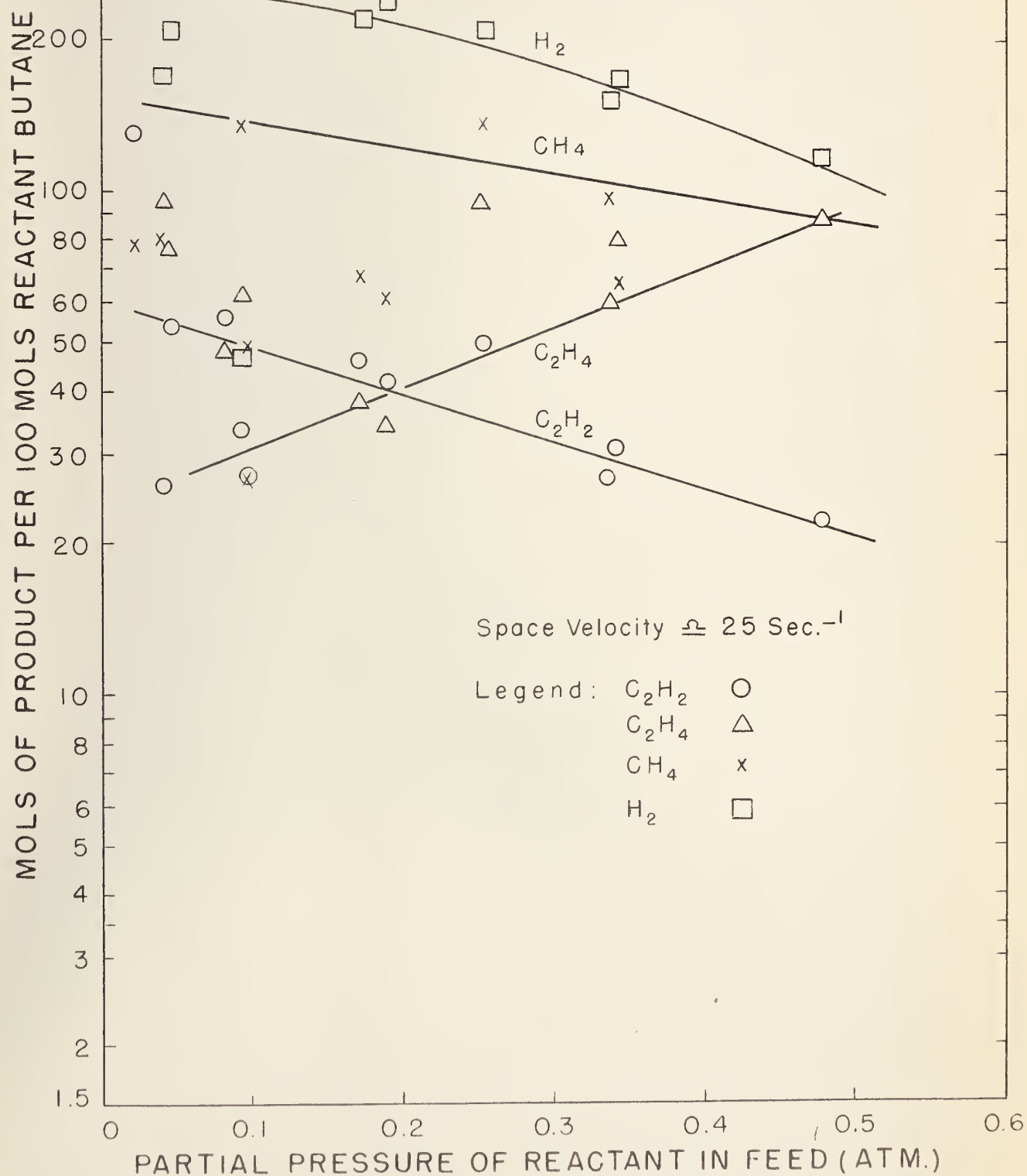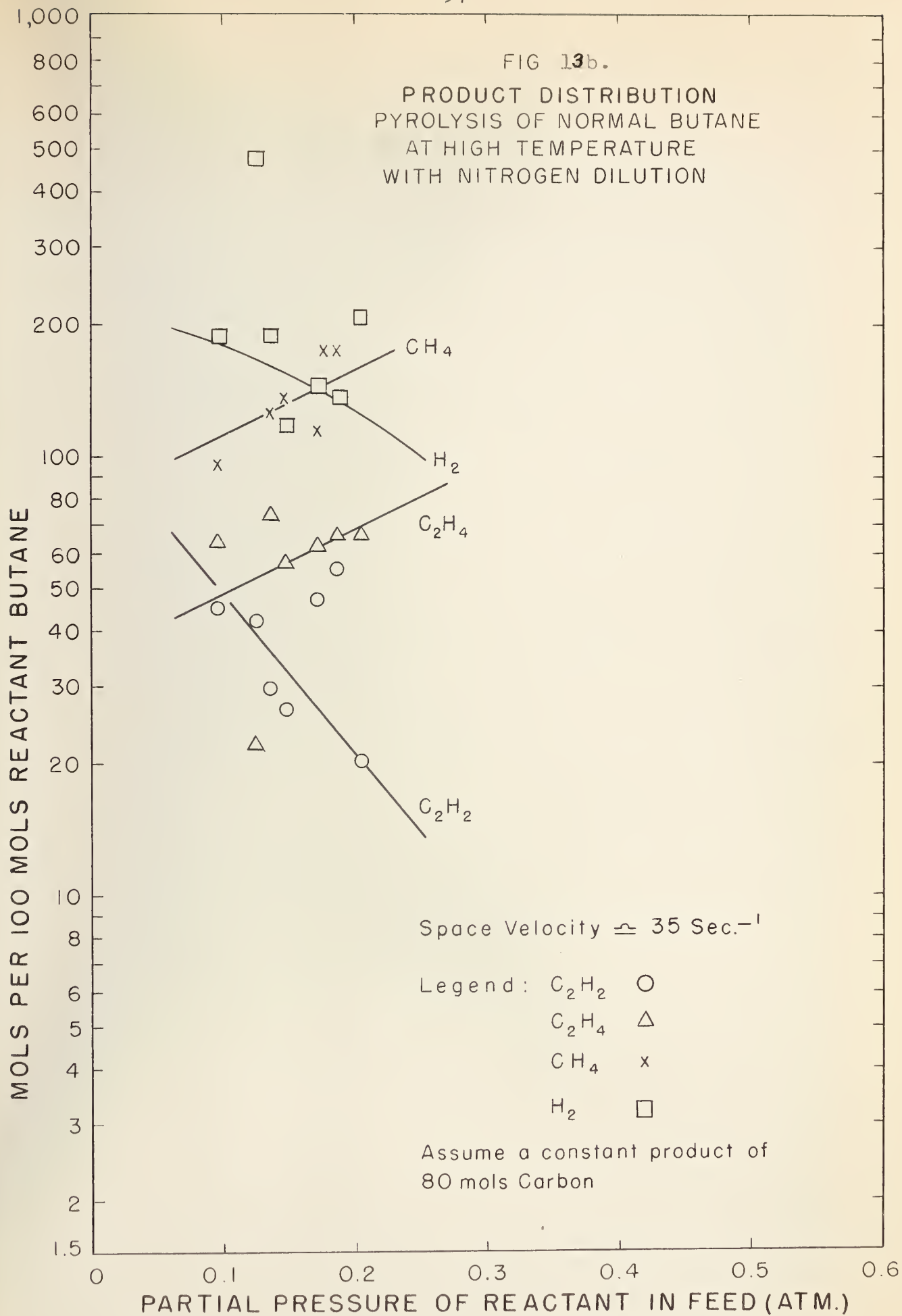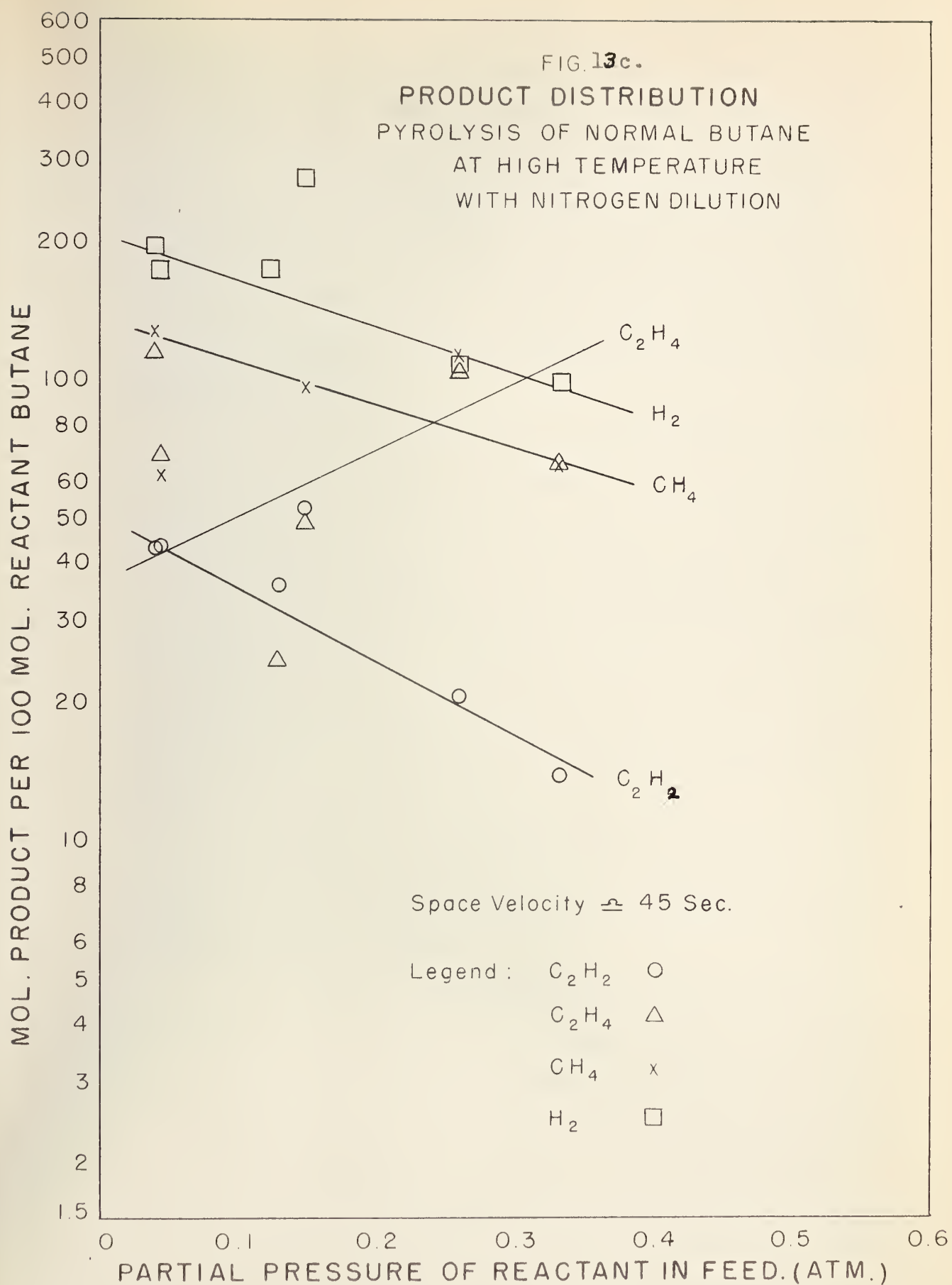
The data were adjusted to a basis comparable to the pyrolysis using nitrogen dilution by subtracting the products of a similar pyrolysis of the natural gas diluent. The products of decomposition were plotted on Figs. 14 and 15 in a manner similar to that for the nitrogen dilution. In Figure 14, product yields are based on the butane feed; in Figure 15, on the butane reacted. A summary of the calculation is presented in Appendix A, Table 6.

Acetylene yields were of the same order as those reported for nitrogen dilution, and showed a similar sensitivity to partial pressure. The ethylene curve was approximately 80 moles higher than its nitrogen counterpart, varying from 120 to 200 moles per 100 moles of butane. A summation of acetylene and ethylene yields accounted for about 85 percent of the butane reacted. The fractional yields of carbon and methane were apparently quite low.

Details of the computations and tabular summaries are included in Appendix A, Sections a, b, c, d and e; Tables 5 and 6.

To examine the reaction on the basis of thermodynamic considerations, product ratios of acetylene and methane were computed (Appendix A, Section f, Table 7), and are shown on Fig. 16a and 16b for nitrogen dilution, Fig. 17 for natural gas dilution. The acetylene to ethylene ratio approximately parallels the curve computed

FIG. 14.

PRODUCT DISTRIBUTION
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NATURAL GAS DILUTION

FIG. 15.
PRODUCT DISTRIBUTION
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NATURAL GAS DILUTION

Legend: C_2H_2 O
        C_2H_4 △
        CH_4 x
        H_2 □
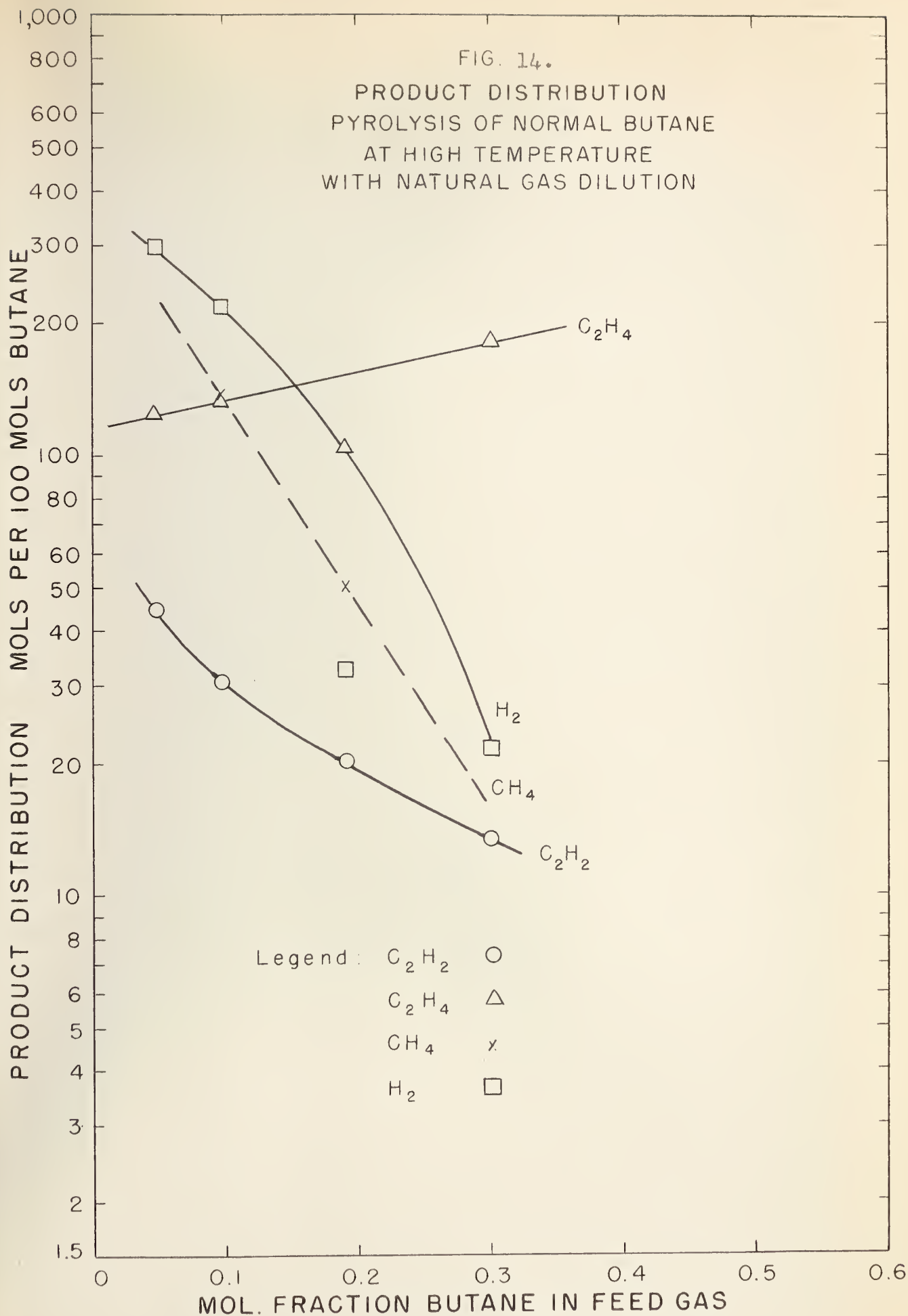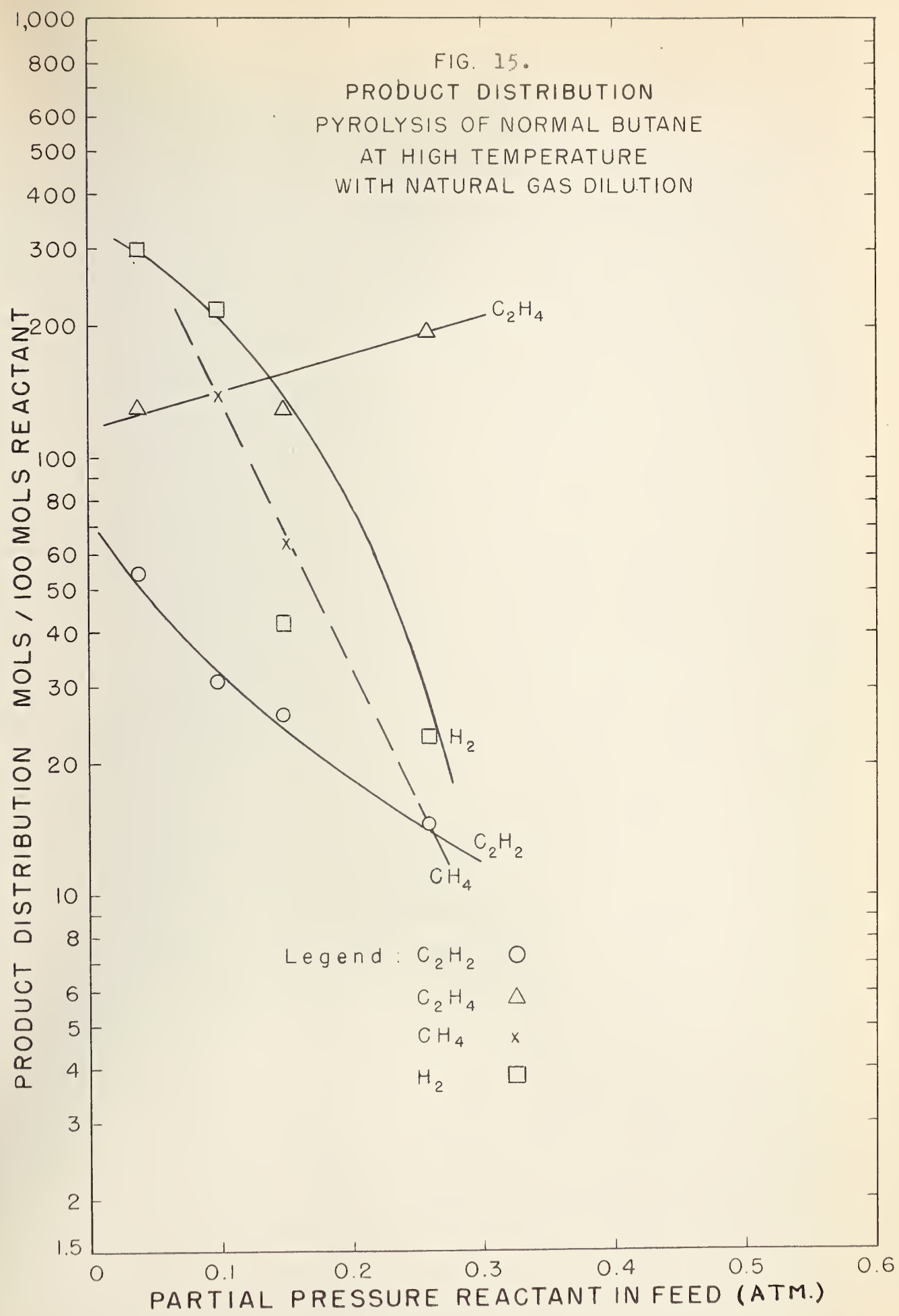
for equilibrium at 2400°F, and deviates progressively
from the theoretical as the space velocity is increased.
The magnitude of the ratio is 1/3 to 1/10 of the equi-
librium ratio and product ratios for acetylene-to-
methane were computed at 2400°F for the observed data,
and plotted on Figs. 16 and 17. A scale change on Fig. 17
should be noted. The approach to the acetylene-methane
equilibrium concentration is much less, the experimental
ratios being several orders of magnitude lower than the
equilibrium values. An even greater deviation from the
equilibrium ratios was noted when natural gas was used
as a diluent, the acetylene-to-methane ratio being about
4 orders of magnitude smaller than the equilibrium ratios.

      The yield of the products ethylene and acetylene
from the pyrolysis with nitrogen are shown in Fig. 18
and 19 (Appendix A, Table 3). Ethylene yields were
found to be favored by a higher concentration of butane
in the feed gas, decreased approximately 40 moles per
100 moles equivalent yield from 60 moles to 20 moles
over a drop of 0.4 atmospheres partial pressure of butane
in feed. On the other hand, the acetylene yield was
increased by 20 moles per 100 moles equivalent from 15
moles to 25 moles over the same range of pressure.
Acetylene was favored by longer contact times within
the range in question, although there is some doubt as
to the actual slope and location of the 35 sec.$^{-1}$ curve
on the graph. It was felt that the relation would

FIG. 16a.
PRODUCT RATIOS
ACETYLENE TO ETHYLENE
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NITROGEN DILUTION

FIG. 16b.
PRODUCT RATIOS
ACETYLENE TO METHANE
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NITROGEN DILUTION

FIG. 17.
PRODUCT RATIOS
ACETYLENE TO METHANE
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NATURAL GAS DILUTION

FIG.18.

ACETYLENE AND ETHYLENE YIELDS
PYROLYSIS OF NORMAL BUTANE
AT HIGH TEMPERATURE
WITH NITROGEN DILUTION

35 Sec.$^{-1}$ (2,600°F.)

45 Sec.$^{-1}$ (2,550°F.)

25 Sec.$^{-1}$ (2,600°F.)

ETHYLENE YIELDS

PARTIAL PRESSURE OF REACTANT BUTANE IN FEED

ACETYLENE YIELDS

35 Sec.$^{-1}$

25 Sec.$^{-1}$

45 Sec.$^{-1}$

PRODUCT YIELD MOLS PER 100 MOLS C EQUIVALENT REACTANT

PARTIAL PRESSURE OF REACTANT BUTANE IN FEED (ATM.)

FIG. 19.
ACETYLENE AND ETHYLENE YIELDS
PYROLYSIS OF NORMAL BUTANE AT
HIGH TEMPERATURE
WITH NATURAL GAS DILUTION
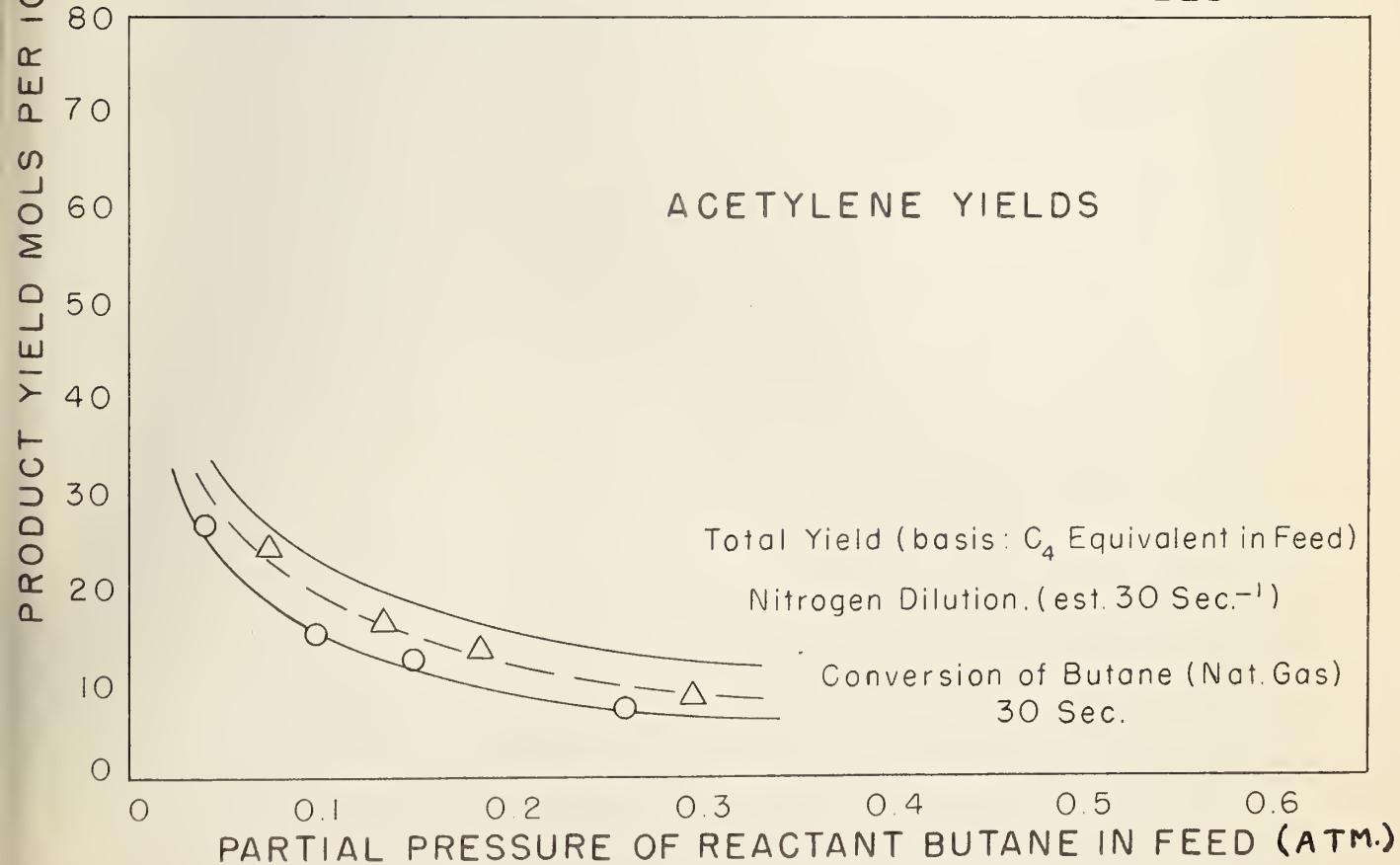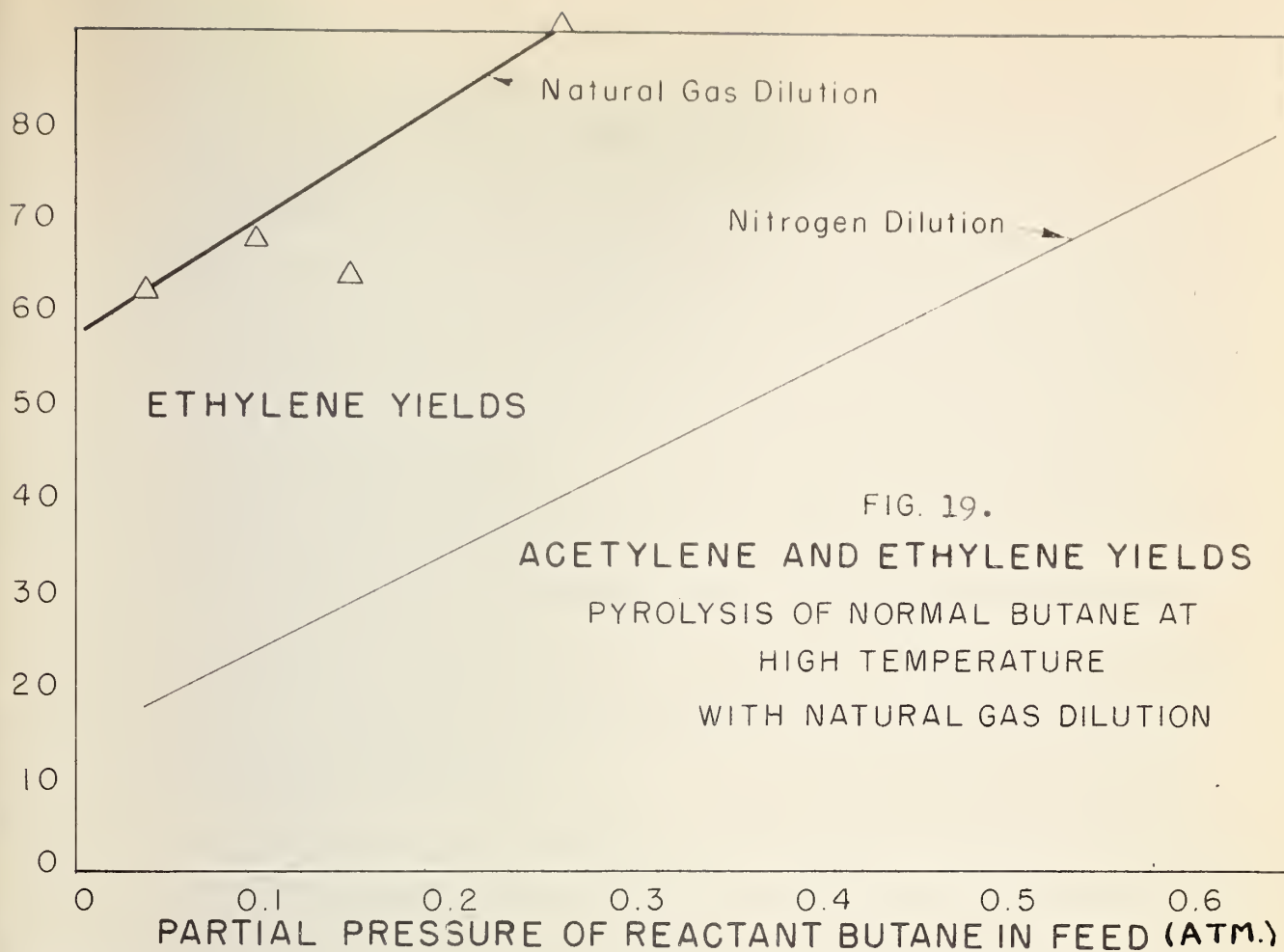
probably be similar to that shown.

Dilution of the reactant gas with natural gas rather than nitrogen (Fig. 19; Appendix A, Table 6) increased the yield of ethylene about 40 to 50 percent from 0.1 to 0.4 atmospheres partial pressure to about 70 to 115 moles over the pressure range, while maintaining the acetylene yield near the same values (23 to 8 moles per 100 moles). On the basis of added butane alone, the yields of acetylene were reduced about 8 moles per 100 moles equivalent, but on the basis of butane equivalent reacted to product, the yield was held within 2 or 3 moles per 100 moles equivalent of that using nitrogen dilution.

VII Conclusions

The products of pyrolysis of butane at high temperature and reduced partial pressure were found to be ethylene, acetylene, methane, carbon and hydrogen. Ethylene and acetylene are the most promising for commercial exploitation. Some very small quantities of tarry substances were formed at the higher concentrations, but were present in insignificant quantities. For the most part there was no polymerization.

Space velocity has an effect on pyrolysis that is complementary to that of temperature; a decrease in space velocity will increase the severity of cracking conditions. Space velocity and dilution also have something of an inverse effect, although the effect was not so pronounced. A high dilution tended to shift the decomposition towards higher acetylene yields.

Dilution with a highly radiant absorbent gas, methane, increased the yield of ethylene and held the acetylene yield at the same general level as found with a transmittant gas, nitrogen, although there is some evidence that the pyrolysis temperature was lower (Appendix A, Section g.). The total yield of unsaturated products represented about 85 percent of the possible, and compared favorably to a commercial scheme proposed by Hasche (8) (9), which yielded about 75 percent of the possible for a similar installation to produce a combined product. The discrepancy may be due to reaction of

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FIG. 20.

RELATION BETWEEN PRODUCT YIELD AND DECOMPOSITION MEASURED BY EXPANSION RATIO

PYROLYSIS OF BUTANE AT HIGH TEMPERATURE
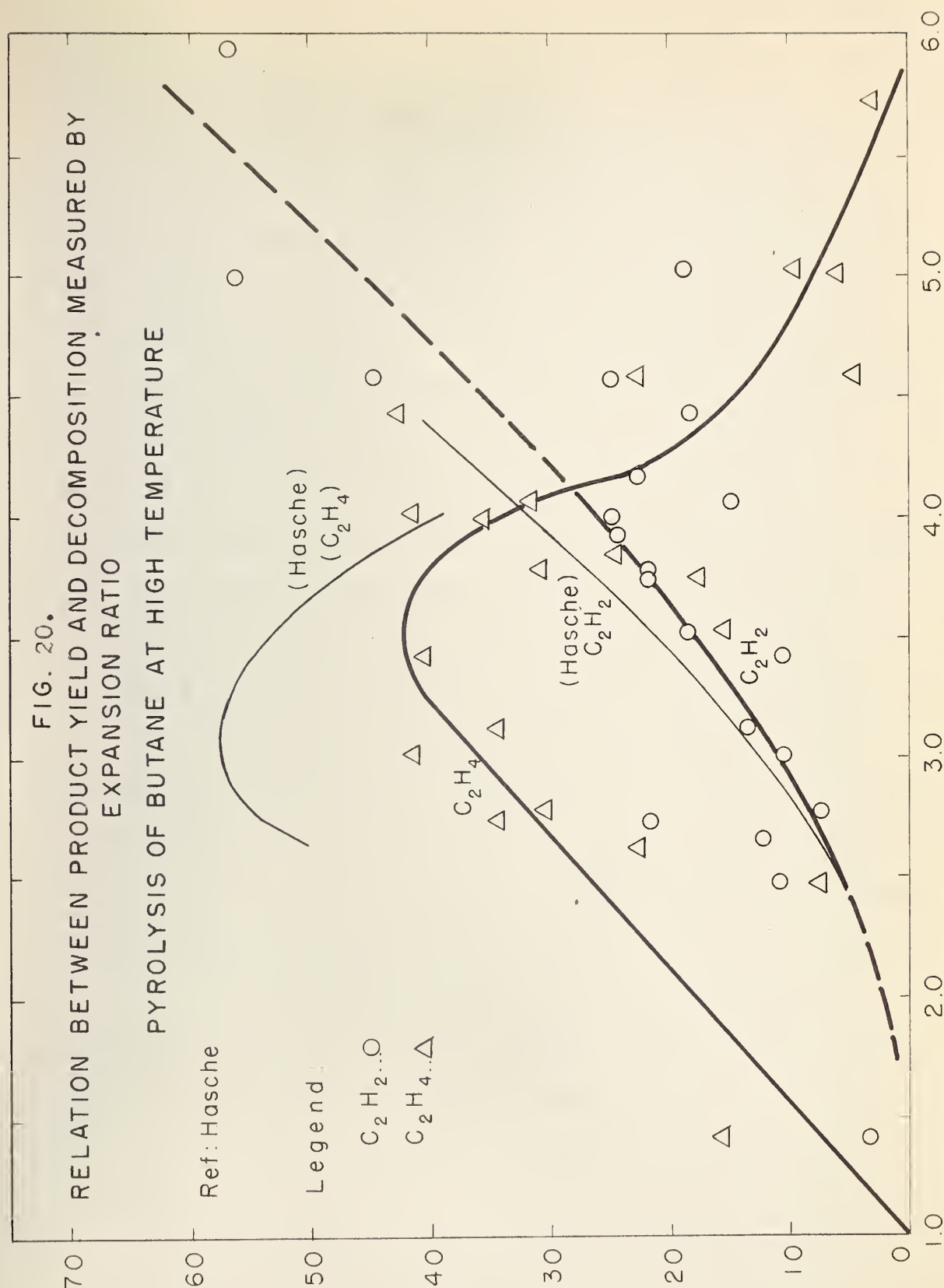
Hasche's product gases with the steam diluent. A

graphical comparison of the Hasche data with that

obtained in this investigation is shown on Fig. 20.

Hasche obtained his data using steam as a dilution

agent, at a ratio in the order of 8 to 1 steam to butane.

The yields of acetylene reported in the present study

for nitrogen dilution are in the same order within the

practical operating range, while the ethylene yields are

somewhat lower. If the pyrolysis in the presence of

natural gas rather than nitrogen is considered, an

increase over Hasche's data to about 80 moles of ethylene

is found from the equivalent butane feed. The total

yield of unsaturates from added butane was found to

approach 85 to 90 percent compared to about 70 percent.

An installation recently commissioned by the

Koppers Co., described by Farnsworth (4) makes use of a

regenerative type furnace similar to the Wulff process.

Yields are in the same order as those reported by Hasche.

Total conversions are in the order of 60 to 75 percent.

Acetylene-to-ethylene product ratios were

found to approach much more closely those at equilibrium

than the acetylene-to-methane ratios. This fact leads

to the conclusion that one of two effects are taking

place:

a. The reaction to form methane is much

faster than that to form ethylene, or

b. The formation of acetylene is a secondary

reaction involving either a molecule of ethylene or two molecules of methane.

At lower temperatures it has been shown that the formation of methane from butane, or ethylene from butane proceed at comparable rates; but as temperature was increased, it was shown by Hague and Wheeler (10) that the decomposition to ethylene becomes predominant. Hasche showed that if a recycle stream included ethylene, there was a quantitative conversion of the ethylene to acetylene (8) (9). It becomes evident, then that the formation of acetylene at these high temperatures proceeds through an intermediate two-carbon compound.

From bond energy considerations, it seems unlikely that the formation of acetylene through an intermediate methane stage would be appreciable while there were higher hydrocarbons present.

Although there is little doubt that free radicals are formed to some extent during the high temperature pyrolysis of hydrocarbons, it is thought that the kinetics may be satisfactorily explained by the decomposition path:

$$C_4H_{10} \rightleftharpoons C_2H_4 + C_2H_6$$
$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$
$$C_2H_4 \rightleftharpoons C_2H_2 + H_2$$

or

$$C_4H_{10} \rightleftharpoons C_3H_6 + CH_4$$
$$C_3H_6 \rightleftharpoons C_2H_2 + CH_4$$

For processes requiring the transfer of as large a quantity of heat as this operation, the utility of the process is limited by heat transfer considerations. The capacity of the equipment to deliver thermal energy to the gaseous reactant will to a large extent determine the products of decomposition. If an intermittent heat source is used, as in the Wulff-Koppers Hasche processes, then the limitation of production is the time required to reheat the checkerwork, roughly three times the pyrolysis cycle. For the installation reported by Farnsworth, the heat transfer to the pyrolysing gases approximated 300,000 BTU per cubic foot of refractory; about 10,000 BTU per square foot of transfer surface. The temperature drop was in the order of $150^\circ F$.

Where a continuous heat source is applied to the reactant through a wall, the limitations become the transmitting qualities of that wall. The values shown in Table 1 illustrate the extent of this problem in the present study. Using an inert non-receiving gas the heat load was found to average approximately 35,000 BTU per square foot of heat transfer surface, a large portion of which takes place over the inlet third of the reactor tube. If a radiation absorbent gas were used, the heat load would be higher, and in the case of natural gas, would approach 85,000 BTU per square foot of transfer area, a much greater load than that encountered by Farnsworth.

Temperature drop across the wall of the silicon carbide tube was calculated to be from 100 to 200°F, depending on the heat load. Approximate calculations of the gas temperature using the fourth power law and assuming equal absorptivities in the gases indicate an additional temperature drop to the gas of about 150°F when natural gas is used as a diluent. The total temperature drop from the fire chamber surface to the pyrolysis gas would then be in the order of 350°F.

Table 1

Heat Load Conditions

Pyrolysis of Normal Butane at High Temperature

Space velocity 30 sec.$^{-1}$

Butane % in Feed: 13.9

Feed at 70°F, 13.5 psia

Data from Appendix A, Section g.

Diluent	Nitrogen	Natural Gas
Gas Temp. (assumed) °F	2400	2400
Heat load (BTU/ft.^{2})	35,000	85,000
Thermal Conduct. (BTU/ft.^{2} °F in.)	109	109
Tube Thickness (in.)	3/8	3/8
Temp. drop across tube wall, °F	123	247
Inner tube temp. (°F)	2475	2350
Approx. Gas Temp.* (°F)	2300-2425	2200-2300

Temperature variations during the determinations with nitrogen dilution could be demonstrated in a similar

*These temperatures were estimated from heat transfer considerations.

manner, since, if the concentration of butane in the feed were doubled, the heat load would be increased greatly, with a resulting drop in gas temperatures. Since a relatively small temperature deviation in the gas would have a pronounced effect on the acetylene-to-ethylene product ratio, this may to some extent explain the apparent effect of partial pressure. The natural gas data were thought to give more comparable results, since a change in butane concentration results in a relatively small change in total heat load.

In addition to heat load, the tendency of the reactor tube to become plugged with carbon deposits imposes another limitation on the process. It is evident, nevertheless that a process of this type operating on an intermittent cycle could be used to pyrolyse butane in a natural gas stream on a basis not unfavorably competitive with that of the Wulff process.

Expressed as percent possible yield at a partial pressure of 0.1 atmosphere, the data show that products were formed from the added butane according to the following:

Table 2

Range of product formation at 0.1 Atmosphere
Partial Pressure of Reactant
Percent Theoretical

	Nitrogen Dilution	Natural Gas Dilution
C_2H_2	10-25	26
C_2H_4	15	70

The difference from 100 percent indicated the extent of conversion of reactant to methane and carbon. The product gases other than ethylene and acetylene would have market value as fuel, since a heating value in the order of 850 B.T.U./ cf could be expected, (Appendix A, Section h.).

Solvent adsorption, hypersorption by carbon, oil absorption or compression refrigeration can be used to separate ethylene and acetylene from the gas stream. Economically, the key to acetylene production is in the purification step.

Silicon carbide, the material from which the reactor was constructed, besides having a fairly high mechanical strength at high temperature, has the highest thermal conductivity of any available ceramic material. This fact in conjunction with the fact that high temperature drop through the tubing wall creates a tremendous stress within the tube indicates that the experimental unit was operating near its maximum capacity. It is felt that a system requiring the transfer of large quantities of heat through a ceramic wall is limited practically, and should, where possible be avoided.

It was thought that the plant investment cost for a process using a continuous heat source would be comparable to the Wulff process, however, due to high refractory failures, the regenerative type furnace has gained favor. The low concentration of product acetylene

and ethylene in the pyrolysis gas stream would increase the separational costs, unless a dilution gas such as steam were used. It was found that the acetylene concentration in the off gas stream was somewhat less than that from the Sachsse process, but recovery of ethylene would increase the value of the off gases, in the same manner as for the Wulff or Koppers-Hasche process.

The conclusions reached in this study may be summarized as follows:

1. The pyrolysis of butane at high temperatures and low partial pressures, produced high yields of ethylene and acetylene. The production of other unsaturates and aromatics was very small.

2. Acetylene was produced through an intermediate two-carbon compound, from ethylene.

3. A process for the manufacture of a combined acetylene and ethylene product by the high temperature pyrolysis of butane in a natural gas stream could be devised. Product yields would exceed those reported for commercial processes, but low concentration in the product stream would add considerably to separational costs.

It is recommended that further research be undertaken to investigate the feasibility of a continuously operating reactor to utilize butane, and/or other natural gas compounds for the production of ethylene and acetylene. The relative effects of

dilution with other gases, such as carbon dioxide and steam would aid in evaluation of the process as a whole, but it is felt that the program should be directed towards use of a natural gas stream rich in ethane, propane and butane, since the costs of ordinary gas processing would allow credit towards installation of these facilities.

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APPENDICES

A. Calculations and Results.

B. Experimental Procedures.

Appendix A

Calculations and Results

a. Material Balances:

Since air was often introduced during
sampling or transfer of the sample to the orsat
analyser, it was necessary to correct the analysis

$$m = \frac{n}{100 - (100/21)n_o}$$

$$M = m'E$$

but nitrogen may not have been entirely removed from
the reactor:

If

$$M'_n = F_n$$

$$M = \frac{M'E}{E - (M'_n - F_n)}$$

Then for carbon balance

$$MC = FC$$

For hydrogen balance

$$Mh = Fh$$

Expansion of hydrocarbon

$$E = \frac{100E - M_N}{F_c}$$

Expansion of Reactants

$$E_c = \frac{100E - M_N}{F_c - M_c}$$

b. Energy Balances:

$$\triangle H_r = \Sigma mH - \Sigma fH$$

On the basis of reactants

$$\triangle H_R = \frac{\triangle H_r}{(F_B - M_B)/f}$$

c. Product yield

$$y_2 = \frac{M_2}{fC/2}$$

$$y = \frac{M_1}{fC}$$

$$Y = \frac{M}{fC/4}$$

d. Partial pressure of products

$$p = m \, (760/700) \text{ atmospheres}$$

e. Product Ratio:

$$\frac{M_a}{M}$$

Table 1

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Summary of Data for the Pyrolysis of Normal Butane at High Temperature
with Nitrogen Dilution

Experimental Run No.	BL-1	BL-7	BL-8	BL-9	BL-10	BL-11	BL-12	BL-13	BL-14
Apparent Temp. $^\circ$F	2150	2660	2650	2630	2560	2550	2525	2550	2740
Run Time (min.)	23	3.30	4.33	4.37	6.17	5.44	4.47	4.41	4.13
Space Velocity (sec. $^{-1}$)	30	26.8	27.6	27.1	43.4	49.1	52.0	48.3	25.5
Feed Composition									
Butane Mol.%	100	54.2	38.9	22.3	17.0	23.2	40.5	51.6	13.8
Nitrogen Mol.%	0	45.8	61.3	77.7	83.0	76.8	59.5	48.4	76.2
Expansion $\left(\dfrac{\text{Vol. Cracked Gas}}{\text{Vol. Feed Gas}}\right)$		2.120	1.942	1.564	1.300	1.345	1.720	1.678	1.131
Gas Analysis $\left(\dfrac{\text{Moles}}{100 \text{ Moles Feed}}\right)$									
CO_2	–	–	–	–	–	–	–	4.2	.67
CO	–	1.4	.9	.8	.8	.5	.8	.6	1.1
N_2	–	47.6	61.3	77.7	66.9	76.8	59.3	48.4	76.2
H_2	12.3	59.6	58.2	48.5	35.7	24.5	30.8	35.8	4.6
CH_4	1.5	44.8	37.2	12.5	12.5	–.	33.0	23.9	14.3
C_2H_2	–	11.3	10.4	8.4	6.8	5.0	5.8	5.0	3.3
C_2H_4	4.5	44.7	23.5	6.8	6.2	3.4	30.2	23.9	6.1
C_2H_6	–	–	–	–	–	5.4	–	–	–
C_3H_6	9.2	–	–	–	–	3.7	–	–	–
C_3H_8	–	–	–	–	–	3.3	–	4.4	–
C_4H_8	–	–	–	–	–	0.4	–	6.6	–
C_4H_{10}	82.0	2.5	2.4	1.8	1.05	9.2	12.4	15.6	3.8
Carbon Black	–	43.5	30.0	35.6	1.3	1.4	.7	4.7	8.4
	110.0	255.5	224.2	192.0	131.3	135.9	172.7	172.5	121.5
Balances: (Gain)									
Carbon %		-2.0	-4.2	-3.2	-44.0	-6.0	-3.6	-6.9	2.3
Hydrogen %		-3.4	4.0	-6.3	0	5.5	6.1	0	-1.9
Expansion:									
of Hydrocarbons		3.02	3.43	3.53	4.59	2.48	2.78	2.32	2.67
of Reactants		3.14	3.60	3.75	4.87	3.46	3.58	2.91	3.30
Energy Requirements MBTU/Mol.C_4 Reacted		186	192	194	190	251	207	242	164

Table 1

Summary of Data for the Pyrolysis of Normal Butane at High Temperature
with Nitrogen Dilution

Experimental Run No.	BL-16	BL-17	BL-18	BL-19	BL-20	BL-21	BL-22	BL-23	BL-24
Apparent Temp. °F	2420	2440	2610	2600	2550	2860	2600	2475	2350
Run Time (min.)	5.03	4.67	4.30	4.16	4.92	6.00	5.00	6.00	5.50
Space Velocity (sec. -1)	24.5	28.6	29.6	29.9	29.4	40.5	35.5	35.9	37.3
Feed Composition									
Butane Mol.%	42.2	30.1	19.6	10.0	5.25	4.84	10.51	14.51	18.4
Nitrogen Mol.%	57.8	69.9	80.4	90.0	94.75	95.16	84.47	85.49	81.6
Expansion $\left(\frac{Vol.\ Cracked\ Gas}{Vol.\ Feed\ Gas}\right)$	1.941	2.040	1.544	1.285	1.158	1.084	1.311	1.445	1.513
Gas Analysis $\left(\frac{Moles}{100\ Moles\ Feed}\right)$									
CO_2	3.3	1.3	3.1	.6	.6	.2	.8	–	2.0
CO	2.7	.2	2.0	.1	.2	.5	.2	2.7	.9
N_2	57.8	70.0	80.8	90.0	94.8	95.2	89.5	85.5	81.6
H_2	61.0	56.0	39.8	22.2	10.0	8.2	19.3	26.6	26.2
CH_4	23.8	37.2	12.3	5.0	3.6	3.0	9.9	14.9	21.2
C_2H_2	11.2	10.9	8.5	4.9	2.6	2.1	4.7	4.3	8.0
C_2H_4	29.0	25.6	6.9	4.1	3.7	3.3	6.7	10.5	11.4
C_2H_6	–	–	–	–	–	–	–	–	–
C_3H_6	–	–	–	–	–	–	–	–	–
C_3H_8	–	–	–	–	–	–	–	–	–
C_4H_8	–	–	–	–	–	–	–	–	–
C_4H_{10}	5.3	2.8	1.0	1.2	.3	.4	–	–	–
Carbon Black	6.8	4.3	5.5	2.6	1.4	.8	.1	1.5	2.1
	200.8	208.3	159.9	131.1	117.2	109.2	131.2	146.0	153.4
Balances: (Gain)									
Carbon %	-18.2	5.8	-26.8	-22.2	-8.6	-12.9	-19.7	-11.7	≠2.9
Hydrogen %	-4.6	4.0	-6.4	2.6	1.5	≠.6	8.8	12.7	59.5
Expansion:									
of Hydrocarbons	3.23	4.44	3.75	3.85	4.00	2.74	4.16	4.06	3.78
of Reactants	3.56	4.81	3.91	4.24	4.18	2.88	4.16	4.06	3.78
Energy Requirements MBTU/Mol. C_4 Reacted	179	216	171	220.5	183	233	197	180	168

Table 1

Summary of Data for the Pyrolysis of Normal Butane at High Temperature
with Nitrogen Dilution

Experimental Run No.	BL-25	BL-27	BL-28	BL-29	BL-30	BL-32	BL-33	BL-34
Apparent Temp. ^{O}F	2500	2400	2440	2625	2670	2550	2600	2660
Run Time (min.)	7.60	3.00	4.50	5.67	8.00	5.02	6.87	7.25
Space Velocity (sec. $^{-1}$)	21.9	32.6	46.9	16.9	17.4	37.2	36.8	38.2
Feed Composition								
Butane Mol.%	2.62	15.1	5.06	10.9	4.3	22.0	16.5	2.01
Nitrogen Mol.%	97.38	74.9	94.9	89.1	95.7	78.0	83.5	98.0
Expansion $\left(\dfrac{\text{Vol. Cracked Gas}}{\text{Vol. Feed Gas}}\right)$	1.118	1.509	1.100	1.315	1.062	1.560	1.412	1.069
Gas Analysis $\left(\dfrac{\text{Moles}}{\text{100 Moles Feed}}\right)$								
CO_2	.6	.6	.2	1.1	.5	.9	-	-
CO	-	2.0	1.8	.9	2.5	1.5	1.3	.3
N_2	92.4	74.9	86.8	90.7	87.4	76.0	83.5	98.0
H_2	12.6	62.8	8.4	28.0	7.2	45.2	18.1	2.7
CH_4	1.8	.4	5.5	5.2	3.4	13.5	21.1	3.5
C_2H_2	3.0	5.6	1.9	2.8	1.1	4.4	4.1	1.1
C_2H_4	.1	2.9	4.6	2.8	4.0	14.4	8.8	1.3
C_2H_6	-	-	-	-	-	-	-	-
C_3H_6	-	-	-	-	-	-	-	-
C_3H_8	-	-	-	-	-	-	-	-
C_4H_8	-	-	-	-	-	-	-	-
C_4H_{10}	.3	1.7	.8	.1	-	-	1.0	-
Carbon Black	1.8	15.0	2.0	8.9	.3	2.7	2.3	.1
	113.6	165.9	112.0	140.4	106.5	158.7	143.5	107.0
Balances: (Gain)								
Carbon %	≠16.0	-30.0	5.4	-36.2	-12.0	-35.0	-6.6	≠8.2
Hydrogen %	35	10.6	9.2	6.1	-7.5	-4.0	4.3	33.0
Expansion:								
of Hydrocarbons	7.4	5.04	4.58	3.89	4.40	3.64	3.49	5.45
of Reactants	8.25	5.55	5.25	3.92	4.40	3.64	3.55	5.45
Energy Requirements MBTU/Mol.C_4 Reacted		194	225.2					

Table 2

Product Yield
Pyrolysis of Normal Butane at High Temperatures

Run No.	Mol.% in Feed Gas	Partial Press Butane in 100 Mol Feed Gas	Mols of Gas per 100 Mol Feed Gas	Mol. Product per 100 Mol. Feed Gas				Mols. Product per 100 Mols Butane in Feed			
				Acetylene	Ethylene	Methane	Hydrogen	Acetylene	Ethylene	Methane	Hydrogen
			Space Velocity – 25 Sec. $^{-1}$								
7	54.2	.498	212.0	11.3	44.7	44.8	59.6	20.8	82.4	82.6	110
8	38.9	.358	194.2	10.4	23.5	37.2	58.2	26.7	60.4	95.6	149.5
9	22.3	.205	156.4	8.4	6.8	12.5	48.5	37.7	30.5	56.1	217
14	13.8	.127	113.1	3.3	6.1	14.3	4.6	23.9	44.2	102.5	333
16	42.2	.389	194.1	11.2	29.0	23.8	61.0	26.6	68.8	56.4	144.5
17	30.1	.277	204.0	10.9	25.6	37.2	56.0	36.2	85.0	123.5	186.0
18	19.6	.181	154.4	8.5	6.9	12.3	39.8	43.3	35.2	62.7	203
19	10.0	.092	128.5	4.9	4.1	5.0	22.2	49.0	41.0	50.0	222
20	5.25	.048	115.8	2.6	3.7	3.6	10.0	49.5	70.5	68.5	191
25	2.62	.024	111.8	2.99	.1	1.8	12.6	114	38.6	68.7	481
29	10.9	.101	131.5	2.8	2.8	5.2	28.0	25.7	25.7	47.7	257
30	4.3	.040	106.2	1.1	4.0	3.4	7.2	25.6	93	79	167
			Space Velocity – 35 Sec. $^{-1}$								
22	10.51	.097	131.1	4.7	6.7	9.9	19.3	44.6	63.7	94.1	183
23	14.51	.134	144.5	4.3	10.5	14.9	26.6	29.6	72.2	102	183
24	18.4	.170	151.3	8.0	11.4	21.2	26.2	43.5	62.0	115.2	144
27	15.1	.139	150.9	5.6	2.9	.4	62.8	37.1	19.2	2.6	41.7
32	22	.202	156.0	4.4	14.4	13.5	45.2	20.0	65.5	61.3	205
33	16.5	.152	141.2	4.1	8.8	21.1	18.1	24.8	53.4	129	110
34	2.01	.019	106.9	1.10	1.3	3.5	2.7	54.7	64.7	174	134
			Space Velocity – 45 Sec. $^{-1}$								
10	17.0	.157	130.0	8.4	7.7	15.5	44.3	49.4	45.3	91.1	261
11	23.2	.214	134.3	5.0	3.4	–	24.5	21.6	14.6	?	105.2
12	40.5	.373	172.0	5.8	30.2	33.0	30.8	14.3	74.5	81.5	76.0
13	51.6	.475	167.8	5.0	23.9	23.9	35.8	9.9	47.3	47.3	70.7
21	4.84	.045	108.4	2.10	3.3	3.0	8.2	47.4	68	62	170
28	5.06	.047	110.0	1.85	4.6	5.5	8.4	36.6	91	109	166

Table 3

84

Product Yield
Pyrolysis of Normal Butane at High Temperatures

Run, No.	Mol.% Butane in Feed	Mol. Butane 100 Mol.Feed in Off Gas	Mol.% Reactant in Feed	Partial Press. Reactant in Feed	Mol. Product per 100 Mol. Feed				Mol. Product per 100 Mol. Reactant				Mol. Product per 100 Mols. C2 Equivalent.	
					C_2H_2	C_2H_4	CH_4	H_2	C_2H_2	C_2H_4	CH_4	H_2	C_2H_2	C_2H_4
Space Velocity - 25 Sec. $^{-1}$
7	54.2	2.5	51.7	.476	11.3	44.7	44.8	59.6	21.7	86.5	86.7	115.3	10.9	43.4
8	38.9	2.4	36.5	.336	10.4	23.2	37.2	58.2	26.8	59.6	95.6	149.5	13.4	29.9
9	22.3	1.8	20.5	.189	8.4	6.8	12.5	48.5	41.0	33.2	61.0	237	20.5	16.6
14	13.8	3.8	10.0	.092	3.3	6.1	14.3	4.6	33.0	61.0	143	46	16.5	30.5
16	42.2	5.3	36.9	.340	11.2	29.0	23.8	61.0	30.4	78.6	64.5	165.5	15.2	39.3
17	30.1	2.8	27.3	.252	10.9	25.6	37.2	56.0	39.9	93.7	136	205.0	19.9	46.8
18	19.6	1.0	18.6	.171	8.5	6.9	12.3	39.8	45.7	37.1	66.1	214	22.8	18.6
19	10.0	1.2	8.8	.081	4.9	4.1	5.0	22.2	55.6	45.6	56.9	252	27.8	23.3
20	5.25	.3	4.95	.045	2.6	3.7	3.6	10.0	52.5	74.7	72.7	202	26.2	37.3
25	2.62	.3	2.32	.021	2.99	.1	1.8	12.6	129	4.3	77.5	543	68	2.2
29	10.9	0.1	10.8	.099	2.8	2.8	5.2	28.0	26.9	26.9	48.1	259	13.5	13.5
30	4.3	–	4.3	.040	1.1	4.0	3.4	7.2	25.6	93.0	79	167	12.8	46.5
Space Velocity - 35 Sec. $^{-1}$
22	10.51	–	10.51	.097	4.7	6.7	9.9	19.3	44.7	63.6	94.1	183	22.3	31.8
23	14.51	–	14.51	.134	4.3	10.5	14.9	26.6	29.6	72.4	102.5	183	14.8	36.2
24	18.4	–	18.4	.170	8.0	11.4	21.2	26.2	43.5	62.0	115.2	142	21.7	31.0
27	15.1	1.7	13.4	.123	5.6	2.9	.4	62.8	41.8	21.6	3.0	468	20.9	10.8
32	22	–	22.0	.203	4.4	14.4	13.5	45.2	20.0	65.5	61.4	205	10.0	32.7
33	16.5	1.0	15.5	.143	4.1	8.8	21.1	18.1	26.4	56.7	136	117	13.2	28.3
34	2.01	–	2.01	.185	1.10	1.3	3.5	2.7	54.7	64.6	174	134	27.3	32.3
Space Velocity - 45 Sec. $^{-1}$
10	17.0	1.0	16.0	.147	8.4	7.7	15.5	44.3	52.5	48.2	96.9	277	26.3	24.1
11	23.2	9.2	14.0	.129	5.0	3.4	–	24.5	35.7	24.3	–	175	17.8	12.2
12	40.5	12.4	28.1	.259	5.8	30.2	33.0	30.8	20.6	107.5	117.5	109.5	10.3	53.8
13	51.6	15.6	36.0	.332	5.0	23.9	23.9	35.8	13.9	66.5	66.5	99.5	6.9	33.3
21	4.84	.4	4.8	.044	2.10	3.3	3.0	8.2	43.7	68.7	62.5	172	21.9	34.3
28	5.06	0.8	4.3	.040	1.85	4.6	5.5	8.4	43.0	1 17.	128	195	21.5	58.5

Table 4

85

Product Ratios
Pyrolysis of Normal Butane at High Temperatures

Run No.	Mol.% in Feed Gas	Partial Press. Butane in 100 Mol Feed Gas	Mols off Gas per 100 Mol Feed Gas	Mol. Product Per 100 Mol. Feed Gas				Ratio of Product Concentration in off Gas Acetylene to:			Partial Pressure Hydrogen in Products.
				Acetylene	Ethylene	Methane	Hydrogen	Ethylene	Methane	Hydrogen	
				Space Velocity - 25 Sec. $^{-1}$							
7	54.2	.498	212.0	11.3	44.7	44.8	59.6	.265	.264	.198	.281
8	38.9	.358	194.2	10.4	23.5	37.2	58.2	.443	.279	.179	.300
9	22.3	.205	156.4	8.4	6.8	12.5	48.5	1.24	.672	.170	.309
14	13.8	.127	113.1	3.3	6.1	14.3	4.6	.541	.233	.719	.041
16	42.2	.389	194.1	11.2	29.0	23.8	61.0	.386	.472	.184	.314
17	30.1	.277	204.0	10.9	25.6	37.2	56.0	.426	.293	.195	.275
18	19.6	.181	154.4	8.5	6.9	12.3	39.8	1.23	.692	.220	.257
19	10.0	.092	128.5	4.9	4.1	5.0	22.2	1.20	.981	.220	.172
20	5.25	.048	115.8	2.6	3.7	3.6	10.0	.702	.723	.259	.086
25	2.62	.024	111.8	2.99	.1	1.8	12.6	2.96	1.66	.237	.113
29	10.9	.101	131.5	2.8	2.8	5.2	28.0	1.00	.549	.100	.213
30	4.3	.040	106.2	1.1	4.0	3.4	7.2	.275	.324	.153	.068
				Space Velocity - 35 Sec. $^{-1}$							
22	10.51	.097	131.1	4.7	6.7	9.9	19.3	.700	.475	.244	.147
23	14.51	.134	144.5	4.3	10.5	14.9	26.6	.4 0	.290	.160	.184
24	18.4	.170	151.3	8.0	11.4	21.2	26.2	.700	.377	.303	.173
27	15.1	.139	150.9	5.6	2.9	.4	62.8	1.93	14.0	.08	.417
32	22	.202	156.0	4.4	14.4	13.5	45.2	.305	.320	.098	.290
33	16.5	.152	141.2	4.1	8.8	21.1	18.1	.465	.192	.225	.128
34	2.01	.019	106.9	1.10	1.3	3.5	2.7	.845	.314	.408	.025
				Space Velocity - 45 Sec. $^{-1}$							
10	17.0	.157	130.0	8.4	7.7	15.5	44.3	1.10	.547	.191	.275
11	23.2	.214	134.3	5.0	3.4	–	24.5	1.47	–	.205	.182
12	40.5	.373	172.0	5.8	30.2	33.0	30.8	.192	.175	.188	.179
13	51.6	.475	167.8	5.0	23.9	23.9	35.8	.209	.209	.140	.213
21	4.84	.045	108.4	2.10	3.3	3.0	8.2	.623	.683	.249	.075
28	5.06	.047	110.0	1.85	4.6	5.5	8.4	.402	.336	.220	.076

Table 5

Summary of Data for the Pyrolysis of Butane at High Temperatures with Natural Gas Dilution

Experimental Run No.	Natural Gas	BM-2	BM-3	BM-4	BM-5	BM-6
Apparent Temp °F		2500	2500	2500	2500	2500
Run Time (min.)		4.75	4.24	3.99	4.39	4.78
Space Velocity (Sec; -1)		30	30	30	30	30
Feed Composition						
Butane Mol.%	-	-	4.9	10.5	19.8	29.5
Nat.Gas Mol.%	100.0	100.0	95.1	89.5	80.2	70.5
C_4 Equivalent in Nat.Gas % #	3.8	3.8	3.8	3.8	3.8	3.8
Expansion $\left(\dfrac{\text{Vol. Cracked Gas}}{\text{Vol. of Feed}}\right)$		1.222	1.302	1.342	1.521	1.635
Gas Analysis $\left(\dfrac{\text{Moles}}{100\ \text{Mols. Feed}}\right)$						
CO_2	-	.6	1.8	1.2	.8	5.5
CO	-	2.0	.4	.7	.8	
O_2	2.2	.3	-	-	2.3	.6
N_2	7.8	7.4	7.0	-	12.6	13.9
H_2		34.2	44.6	29.2	33.8	30.5
CH_4	84.5	54.9	45.4	63.4	54.0	33.6
C_2H_2	-	1.8	3.9	4.7	5.4	5.3
C_2H_4	0.9	22.8	26.7	34.6	38.5	71.1
C_4H_{10}	3.8	-	.8	-	4.0	1.7
	100.0	122.2	130.2	134.2	152.1	163.5
Balances (Gain)						
Carbon %		-12.9	13.5	48.5	-.4	45.3
Hydrogen %		-	-2.5	47.7	-2.8	-9.5

All hydrocarbons reported as methane and butane equivalents.

Table 6
Product Yield
Pyrolysis of Normal Butane at High Temperatures with Natural
Gas Dilution

Experimental Run No.	BM-2	BM-3	BM-4	BM-5	BM-6
	Natural Gas	Diluent Free Gaseous Products		Added Butane	
$\left(\dfrac{\text{Mols}}{\text{100 Mols Feed}}\right)$					
H2	-	12.1	22.6	6.5	6.4
CH4	-	-6.8	14.4	9.9	-5.0
C2H2	1.8	2.2	3.2	4.0	4.0
C2H4	22.8	5.1	14.2	20.2	54.7
C4H10	-	.8	-	4.0	1.7
Partial Pressure in Feed:					
Butane	.035	.045	.097	.180	.274
Reactant	.035	.038	.097	.146	.259
Product Yield:					
$\left(\dfrac{\text{Mols}}{\text{100 Mols Butane}}\right)$					
H2		247	215	32.8	22.8
CH4		-	137	50.0	-
C2H2	47.3	44.8	30.5	20.2	14.3
C2H4	600.0	104.0	135	104	194.5
$\left(\dfrac{\text{Mols}}{\text{100 Mols Reactant}}\right)$					
H2		295	215	41.2	22.8
CH4		-	137	62.6	-
C2H2	47.3	53.6	30.5	25.3	14.3
C2H4	600.0	124.2	.35	128.0	194.5
$\left(\dfrac{\text{Mols}}{\text{100 C2 Equivalents}}\right)$					
C2H2 C2H4	23.6	26.8	15.2	12.7	7.2
Product Ratios:					
C2H2 : C2H4	.079	.146	.136	.140	.075
C2H2 : CH4	.033	.086	.074	.100	.158
Partial Press H2 (atm)	.258	.315	.200	.205	.172

f. Thermodynamics:

$$\Delta F_T^O = -RT \ln Ka$$

$$\ln Ka = -\Delta F_T^O / RT$$

$$Ka = \ln^{-1}(-\Delta F / RT)$$

but $Ka = K_p$

For the reaction

$$C_4H_{10} \rightleftharpoons 4C + 5H_2 \qquad ----------\ 1$$

$$K_{p1} = p_h^5 / P_e$$

Similarly

$$C_2H_4 \rightleftharpoons 2C + 2H_2 \qquad ----------\ 2$$

$$K_{p2} = p_h^2 / p_e$$

$$C_2H_2 \rightleftharpoons 2C + H_2 \qquad ----------\ 3$$

$$K_{p3} = p_h / p_e$$

$$CH_4 \rightleftharpoons C + 2H_2 \qquad ----------\ 4$$

$$K_{p4} = p_h^2 / p_m$$
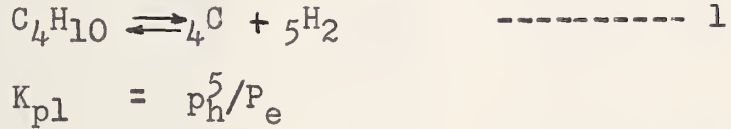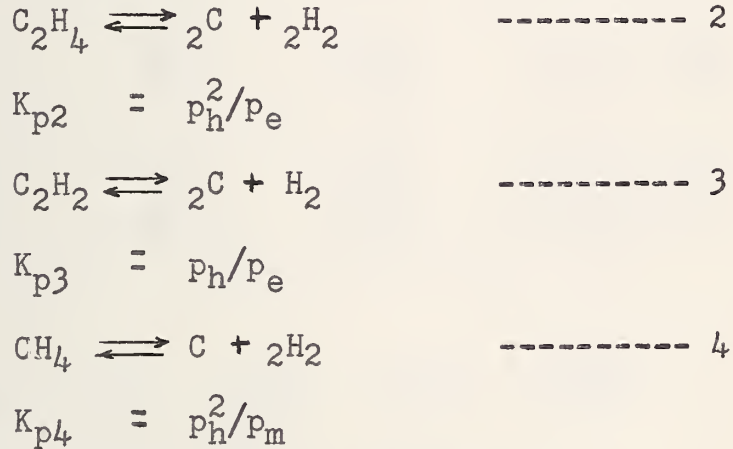
When there is appreciable methane present:

$$2CH_4 \rightleftharpoons C_2H_2 + 3H_2 \qquad ----------\ 5$$

$$K_5 = p_a p_h^3 / p_m^2$$
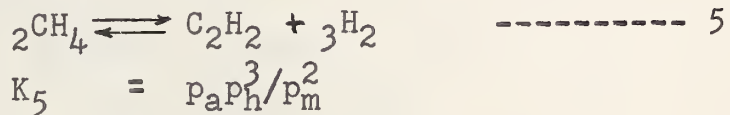
Then if butane is 100% reacted

$$P_e = p_h^2 / K_2 \qquad ----------\ 6$$

$$P_a = p_h / K_3 \qquad ----------\ 7$$

$$p_m^2 = p_a p_h^3 / K_5 \qquad ----------\ 8$$

$$p_a / p_e = (K_2 / K_3) p_h \qquad ----------\ 9$$

$$p_a / p_m = p_m K_5 / p_h^3 \qquad ----------10$$

$\|$

Table 7

Calculation of p_h

Temp. $^{\circ}R$	Reaction	ΔF° K cal.	$\Delta F^{\circ}/-RT$	K_p
2460	2	−50.2	10.39	2.06×10^4
	3	−65.0	13.20	5.42×10^5
	4	−26.1	5.31	2.01×10^2
2660	2	−52.4	9.86	1.92×10^4
	3	−62.2	11.69	1.20×10^5
	4	−31.3	5.89	3.63×10^2
2860	2	−54.6	9.55	1.41×10^4
	3	−60.0	10.49	3.32×10^4
	4	−36.8	6.43	6.17×10^2
3060	2	−57.0	9.31	1.11×10^4
	3	−57.6	9.41	1.22×10^4
	4	−42.1	6.87	9.59×10^2
2260	2	−48.0	10.63	4.14×10^4
	3	−67.4	14.92	3.01×10^6
	4	−20.5	4.54	9.40×10

Summary:

Temp. $^{\circ}F$	2000	2200	2400	2600	Power of 10
K_2	3.06	1.92	1.41	1.11	4
$1/K_2$	3.37	5.21	7.09	9.01	−5
K_3	54.2	1.20	.332	.122	5
$1/K_3$	1.84	8.34	30.1	82.0	−6
K_4	2.01	3.63	6.17	9.59	2
$1/K_4$	4.98	2.83	1.62	1.04	−3

$p_h = P$ since $1 + 1/K_3 \approx 1.00$

P	0.5	0.4	0.3	0.2	0.1	.01	Power of 10
T	$p_e = p_h^2/K_2$			Equation 6			
1800	.605	.389	.218	.0967	.0242	.000242	-5
2000	.842	.539	.303	.135	.0337	.000337	-5
2200	1.30	.834	.469	.208	.0521	.000521	-5
2400	1.77	1.13	.637	.284	.0709	.000709	-5
2600	2.25	1.44	.811	.360	.0901	.000901	-5
	$p_a = p_h/K_3$			Equation 7			
1800	.166	.129	.097	.064	.0332	.00332	-6
2000	.920	.736	.551	.368	.184	.0184	-6
2200	4.17	3.34	2.50	1.67	.834	.0834	-6
2400	15.1	12.0	9.04	6.02	3.01	.301	-6
	$p_a/p_e = (K_2/K_3)\, p_h$			Equation 9			
1800	.0274	.0332	.0433	.0663	.137	1.37	
2000	.109	.139	.182	.272	.760	7.60	
2200	.320	.401	.534	.803	1.60	16.0	
2400	.853	1.06	1.42	2.12	4.25	42.5	
2600	1.82	2.28	3.03	4.56	9.10	91.0	

P	0.6	0.4	0.2	0.1
p_m	$p_a/p_m = K_5 p_m/p_h^3$		Equation 10	
0.8	40.5	136	1090	8730
0.6	30.4	102	816	6560
0.4	20.2	68	545	4360
0.2	10.1	34	272	2180
0.1	5.1	17	136	1090

g. Reactor Gas Temperature.

    1. Heat Transfer Area:

$$\text{log mean area} = \left(\frac{(d_o - d_i)/2.303 \log d_o/d_i)2}{1728 \times 4} \right) L$$

$$\frac{(1.125)^2(30)}{(1728)(4)} = 0.0173 \text{ ft.}^3$$

Estimated gas temperature: $2400°F$.

Reactor Heat Load, basis: 100 moles of feed.

	Feed Composition Mole %		Enthalpy of Gas[1] 70°F. 2400°F. MBTU/lb. Mole	Product Enthalpy	
	F	H		Comp. X%	XH
N_2^2	86.1	0	18	86.1	15.0
H_2			18	20.8	3.8
CH_4			5	18.0	0.9
C_2H_2			128	4.2	5.4
C_2H_4			72	7.9	5.7
C_4H_{10}	13.9-55.0		70	-	---
	100.0			100.0	30.8

Feed Enthalpy: FH   -7.71

            Difference: $H_T - H_t = 37.7$

Space Velocity: 30 sec^{-1}

Feed Rate: $(30)(0.0173) = 0.519 \text{ ft.}^3/\text{sec.}$

                   $= 1870 \text{ ft.}^3/\text{hr.}$ at reactor conditions.

$$\frac{(1870)(520)(13.5)}{(379)(2860)(14.7)} = 0.824 \text{ lb. Moles/hr.}$$

[1](Fig. 22)

Total heat load on the reactor tube:

$$(0.824)(37.7) = 31,100 \text{ BTU/hr.}$$

$k = 109 \text{ BTU/hr.ft.}^2\text{in.}^\circ\text{F.}$ (p.33), $l = 3/8"$, to $= 2600^\circ\text{F.}$

$$Q = (kA/l)(t_o - t_i)$$

$$= (109)(8/3)(0.870)(2600 - t_i)$$

$$\frac{(31100)(3)}{(109)(0.870)(8)} = 2600 - t_i$$

$$t_i = 2600 - 125 = 2475^\circ\text{F}$$

Similarly, the heat load on the reactor tube when natural gas is used as diluent may be calculated.

Heat load on tube: 72.8 MBTU/lb. mole of feed

or 60000 BTU/hr.

Inner surface temperature: 2350°F.

2. By consideration of radiant heat effects, and assuming equal absorptive power in the gases, the relative temperature drop may be computed:

$$\frac{(T_i^4 - T_g^4)_n}{(T_i^4 - T_g^4)_{n.g.}} = \frac{1}{2}$$

$$T_{g_{n.g.}}^4 = T_i^4 - 2(T_i^4 - T_g^4)_n$$

where subscripts n and n.g. denote dilution with nitrogen and natural gas.

If we assume a temperature drop for nitrogen dilution, we may compute the corresponding gas temperature, $^\circ\text{F}$.

T_n	$T_{n.g.}$
2450	2300
2400	2270

Then, since the difference in absorptive powers would increase the deviation shown, using natural gas as a diluent reduces the reaction temperature by about 150°F.

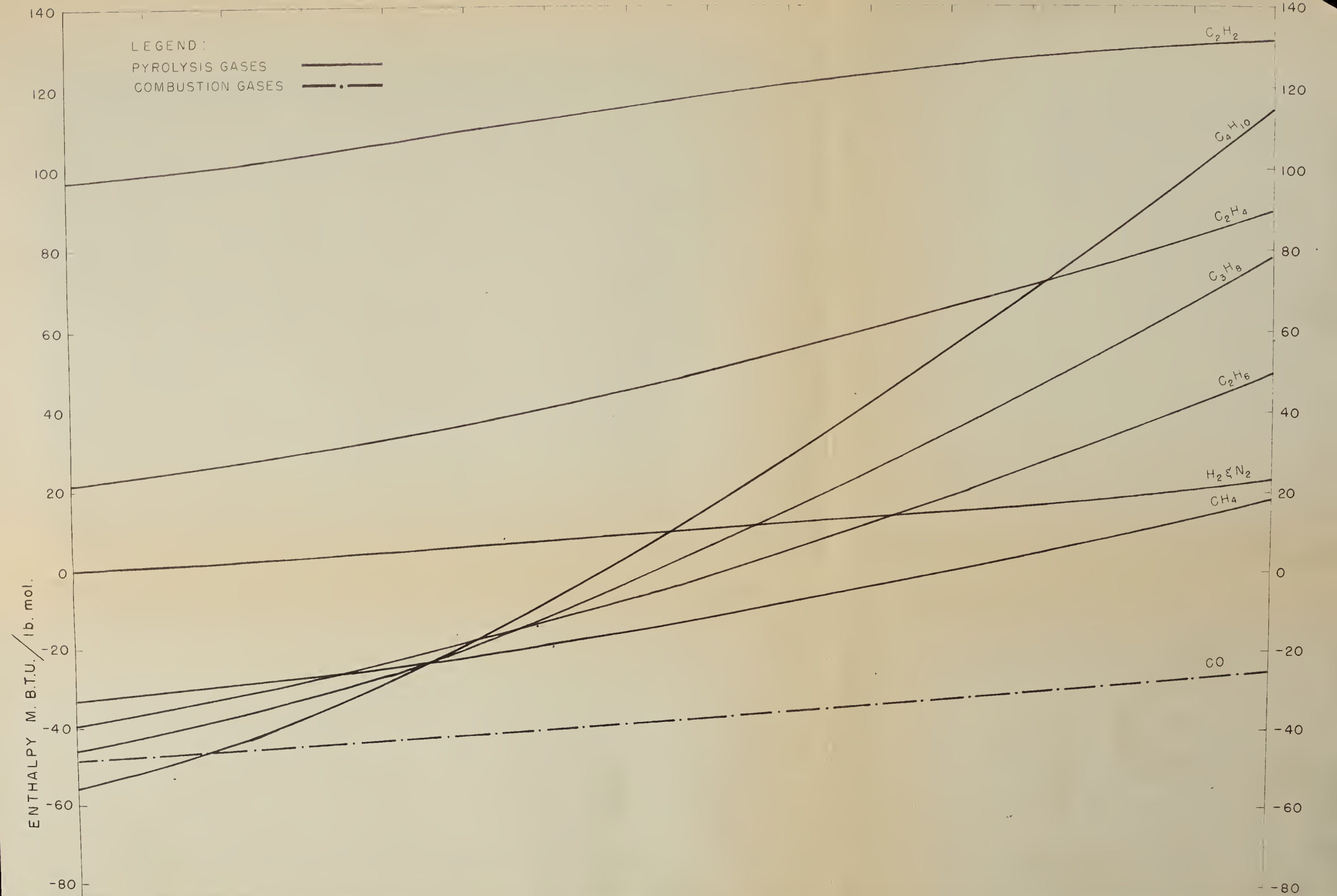h. Comparative Estimates of Heating Values.

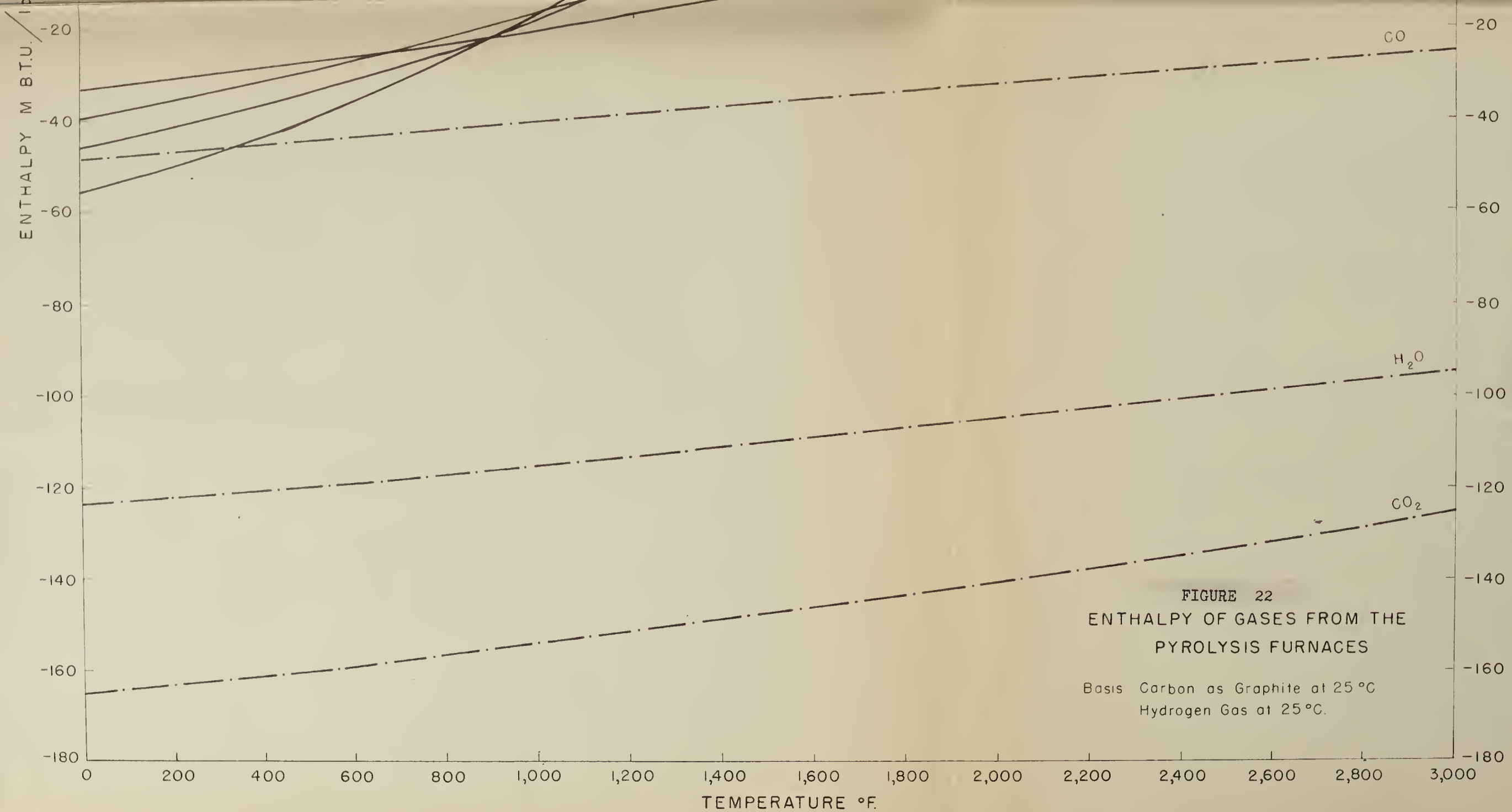| Component	Molal H	Nat.Gas Feed %	Combustion Products		Pyrolysis gas Residue %	Combustion Products	
			Moles	H		Moles	H
CO_2	-163		104	-170	1.2	56	-91
H_2O	-122		190	-230		142	-170
O_2	0	2.2					
N_2	0	7.8	748	0	7	508	0
H_2	0	84.5			29.2		
CH_4	-33				56.4		
C_2H_2							
C_2H_4	-22	0.9					
C_4H_{10}	-57	3.8					
		100.0		-400-30			-264
							-21

H natural gas feed = 370 BTU/lb. mole

$$= \frac{370}{379} = 978 \text{ BTU/ cf.}$$

H Pyrolysis Residue gas $= \frac{240}{0.75}$ BTU/lb. mole.

$$= \frac{240}{(0.75)(379)} = 850 \text{ BTU/ cf.}$$

FIGURE 22
ENTHALPY OF GASES FROM THE
PYROLYSIS FURNACES

Basis Carbon as Graphite at 25 °C
Hydrogen Gas at 25 °C.

Appendix B

Experimental Procedures

1. Reactor Operation

    The heating time required for the reactor furnace to reach operating temperature for the process was more than 24 hours. It was felt that a shorter heating period would lead to excessive thermal shock.

    The following procedure was adopted to allow the body of the furnace to heat at a moderate rate: One burner was lighted at a time; the rate of heating was controlled by the fuel gas rate and the air-gas mixture. First, the steam ejector was started to draw air into the furnace; a quench water flow rate to give a maximum of 4 in. mercury differential across the orifice was set; jacket cooling water was started fully; and the pyrometer port cooling air was started to give an orifice differential of about 4 in. All burners were closed except that immediately below the lighting port. If the furnace body were tight, the pressure would be reduced about 3 cm. water. The lighting port was removed, and the lighting torch inserted.

    A small amount of air was passed through the open burner, directly under the port, and the gas flow was started at a reading of 1.2 on the fuel gas rotameter, Fig. 11, part 6. The burner flame could now be observed at the bottom pyrometer port. If no flame was

visible, the procedure was repeated until successful. The most common difficulty encountered in lighting the furnace was the adjustment of the air rate into the furnace. It was necessary to purge the furnace fire chamber thoroughly before lighting in order to avoid the danger of an explosion from accumulated gases.

Once the flame was clearly visible, a period of about 5 hours was allowed to pass before the second burner was lighted. During this time it was advisable to gradually increase the air to the mixture in order to further stabilize the flame.

When the bottom of the furnace chamber showed signs of becoming red, ($800^{\circ}F$ - $900^{\circ}F$, by thermocouple) the second burner was opened, air to the burners was increased, and the gas readjusted to 1.2 on the rotameter.

A second waiting period of 3 hours was advisable, at which time the remaining burners were opened, and the gas and air rates adjusted. All four burners were alight, and the fuel gas and air rates were higher. The university compressed air could be used further, or the equipment optionally put on the blower supply. If the blower was used, the gas rate should be kept at 2.0 on the rotameter for about 6 hours. If the university supply was used, the gas rate was set at about 1.5 to 1.7 on the rotameter for 6 hours. At this point, the quench water rate should be increased to a maximum 8 in. mercury across the orifice flow-

meter, and the pyrometer port cooling air set at 10 in.
mercury. The final step of the heating cycle was
accomplished in from 12 to 14 hours, during which time
the full blower supply was used. The fuel gas rate
was increased to about 2.8 on the rotameter. A maximum
temperature of 2800°F could be reached with the equip-
ment described.

It was advisable to allow a small amount of
air to flow through the reactor during the heating
cycle. This precaution served two purposes: it
prevented excessive overheating of the reactor tube,
and removed any carbon deposits in the tube by oxidation.

When the desired operating temperature had
been reached, the reactor was thoroughly purged with
nitrogen and, when the initial conditions had been
recorded, the reactor gas flow was started. The
pressure in the reactor was adjusted to the desired
level by means of the air ejector and the reaction
conditions were noted. Pressures and temperatures were
recorded periodically throughout the test. The sampler
was started after about 3 minutes of operation.

Experimental conditions were observed until
the pressure drop across the reactor tube increased
out of proportion or became erratic, indicating plugging
in the reactor tube, at which time the pyrolysis gas was
shut off, and the tube was purged free of air with

nitrogen. The bypass valve to vent (Fig. 6A, part 8) was opened to allow the feed gas stream to pass to atmosphere, and the feed rates were adjusted.

Nitrogen and natural gas rates were set using the calibrated rotameter (Fig. 11, part 5); butane rates were determined by a restored state weighing technique in which a Toledo balance type scale was utilized (Fig. 11, part 8) known weight added to the butane side of the balance and time to restore to the original reading was taken. The approximate butane rates were set, and the final rate was observed independent of the rest of the experiment.

At a prearranged signal, the feed mixture was introduced to the reactor tube and simultaneous readings were taken of the diluent gas meter and off gas meter.

The apparent temperature of the reaction was taken, and the sampler pump started to flush the sample lines. Pressure and pressure drop readings on the control manometer were noted, and a spot check of the off-gas meter rate was taken. Samples were started and another temperature reading was obtained. Pressure readings and pressure drops throughout the components of the equipment were carefully observed for signs of plugging.

When the butane rate had been checked, the

reactor was flushed thoroughly with nitrogen, followed by an air purge to burn clear the carbon depositions. When the pressure drop in the reactor tube was less than 2 cm. water at 6 cu. ft. per minute air flow, the tube was again flushed with nitrogen, and another experiment was started.

The gas sample for acetylene was gathered in a special bulb consisting of two chambers. (Fig. 10, part L). The gas sample (50 ml.) was passed into the upper chamber, displacing a 4:1 ethanol (methanol) 0.1N silver nitrate solution into the lower chamber.

2. Tests and Analyses

Analysis of the product gases for each of the samples taken was made using a Burrell orsat type gas analyser. The solutions were commercial absorbents for the various groups of compounds, as follows:

a. Potassium hydroxide, 20% solution by weight, absorbs acid gases.

b. Sorbent "D", a specific absorbent for acetylene and higher acetylenic compounds.

c. Sorbent "A" for olefins, also absorbs benzene and aromatics, has a slight solubility for hydrocarbons such as propane and butane.

d. Oxsorbent; will absorb oxygen quickly, will take up small quantities of carbon dioxide.

e. Cosorbent for carbon monoxide.

Hydrogen was determined by catalytic oxidation over copper oxide at $300^{o}C$. Small amounts of hydrocarbons were sometimes converted to CO_2, which could then be detected by passing it through the potassium hydroxide solution. Any appreciable amount of hydrocarbon decomposed was considered to be butane if butane was detected during the analysis for paraffins.

Saturated paraffin hydrocarbons were oxidized catalytically to carbon dioxide and water at $380^{o}C$.

Acetylenes were precipitated as silver acetylide from a silver nitrate-alcohol solution. The nitric acid formed was back-titrated with standard

sodium hydroxide to give a quantitative measure of the acetylene present.

In order to provide better control in the analysis for higher olefins and paraffins, it was decided to sample sufficient gases for a fractional distillation analysis by Podbielniak apparatus. Several samples were analysed, none completely satisfactorily due to two factors:

A. The presence of acetylene in the gases (a) formed azeotropic mixtures with both methane and ethylene; and (b) introduced serious operational problems due to the proximity of its freezing point to its dew point.

B. The presence of large quantities of inert gases (nitrogen, hydrogen) and methane made it very difficult to sustain a satisfactory reflux in the column thus the distillation was less than satisfactory.

It became apparent, from the distillation, however, that the quantities of higher compounds present were small, and decreased markedly with higher dilution ratios. What higher compounds were present were primarily butanes. It was felt, then, that an assumption that the hydrocarbons found were methane and butane was in order.

Later in the nitrogen series, another means of analysis, a chromatographic technique became available. The adsorption medium that would give quantitative

separation of components was not available, but there was good evidence that the adsorbents in use would separate ethane, ethylene, acetylene, propylene, propane, butylenes and butane from a mixture. Samples number 31 and 33 from the nitrogen series, and BM-2 from the natural gas series were passed through the column and found to contain no detectable quantity of any hydrocarbon beyond ethylene. (Several other tests had similar results but were in the nature of preliminary tests of the apparatus.) A similar synthetic mixture of natural gas and acetylene showed an appreciable propane peak and a peak for isobutane. These results were taken as confirmation of the preceding assumption, at least for the high dilution ratios.